

STUDIES OF SOME BASIC PARAMETERS IN THE PYROLYSIS GAS CHROMATOGRAPHY TECHNIQUE

Eva Andersson



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by

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Title and subtitle Studies of some Basic Parameters in the Pyrolysis Gas Chromatography Technique			
Abstract The <u>temperature-time profile</u> of a sample (0.5 - 20 µg) placed on a <u>filament pyrolyzer</u> , was determined by studying the rate of degradation of <u>cis-1,4-polybutadiene</u> by sequential pyrolysis. The experimental results were combined with theoretically derived expressions from which the temperature-time profile of different amounts of sample could be calculated. The quantitative analysis was illustrated by pyrolysis of polystyrene, polybutadiene and poly(methyl methacrylate) with ng to mg amounts of sample. The detection limit was seen to be affected by catalysis from the metal filament. The <u>thermal degradation of polystyrene, polybutadiene, poly(methyl methacrylate) and polyacrylonitrile</u> was investigated with pyrolyzer filaments made from <u>iron, nickel and platinum</u> . The composition of the pyrolysis products was independent of the filament metal, but the yields of the products differed. The pyrolysis gas chromatography technique was applied to the analysis of <u>vulcanized natural rubber</u> . The <u>sulfidic crosslinks</u> were studied utilizing a sulfur selective flame photometric detector.			
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Analytical Chemistry
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This thesis is a summary of the following paper which will be referred to in the discussion by roman numerals I - IV.

- I Determination of the Temperature-Time Profile of the Sample in Pyrolysis-Gas Chromatography.

Eva M. Andersson and Inger Ericsson

J. Anal. Appl. Pyrol., 1(1979)27

- II Samples from ng to mg in Pyrolysis Gas Chromatography

Eva M. Andersson and Inger Ericsson

J. Anal. Appl. Pyrol., 2(1980)97

- III A Study of the Thermal Degradation of Organic Polymers with Different Metals of Pyrolysis Filament

Eva M. Andersson and Inger Ericsson

Submitted to J. Anal. Appl. Pyrol.

- IV A Study of Sulfur Linkages in Natural Rubber Vulcanizates by Pyrolysis Gas Chromatography with Flame Photometric Detection

Eva M. Andersson, Inger Ericsson, Lena Trojer

In manuscript

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1. INTRODUCTION

The heating of materials until some degradation occurs has long been utilized to obtain knowledge about the composition. In simple cases the smell of the evolved products can give enough information.

When the thermal degradation is made under controlled conditions, viz. in an inert atmosphere, it is called pyrolysis. Pyrolysis is especially well suited for characterization of unvolatile materials. The technique has found and increasing use in the study of synthetic polymer materials, for which there are few other methods available.

Pyrolysis coupled with infrared spectroscopy, mass spectrometry or gas chromatography are sophisticated analysis systems. At present the two latter combinations are most frequently utilized [13].

In spite of the sophistication of the systems the resulting pyrograms are often greatly dependent on the pyrolysis conditions. A better knowledge of the method is essential in order to get more consistent results between different investigators. This work has therefore involved a study of some of the parameters which were thought to cause these inconsistencies.

The most important parameters include the construction of the pyrolysis head, the heating rate of the pyrolyzer, the pyrolysis temperature and time, the cooling rate and the sample size, [2,3].

To obtain any reproducible pyrolysis results these parameters need to be reproducible. Most of the equipment used today can produce reproducible values. However, most laboratories still have to create their own data banks of pyrolysis results [4], as their results may be different from those of other laboratories.

To rationalize and standardize pyrolysis gas chromatography, correlation trials have been arranged [5,6,7,8,9]. Samples were sent to different laboratories for analysis together with reference substances. Although recommendations about the pyrolysis conditions were given, the result of also the most recent trial was not quite successful [9].

The most important reason for the inconsistencies were traced to the construction of the equipment. There were differences in the materials of the sample holder, the heating times differed and different pyrolysis temperatures were obtained. The actual pyrolysis temperature can be quite different from the nominal temperature of the instrument [10,11]. Furthermore the size of the samples taken by different investigators varied.

2. EQUIPMENT

The foil pulse pyrolyzer used in this work has been developed by Inger Ericsson [2]. The pyrolyzer consists of a metal foil (usually Pt), 0.0125 x 2.6 x 15 mm, mounted between two pairs

of platinum plates. The foil is heated by two current pulses. The first, usually 8 ms, heats the foil to the desired end temperature. The second pulse is lower and it compensates for the heat losses and keeps the foil at the desired temperature. The sum of the length of the pulses gives the total heating time.

The temperature of the foil is determined with a temperature calibrated photodiode and, at low temperatures, from the resistance change of the foil.

The pyrolyzer was mounted at the injection port of a Varian 1860 gas chromatograph, and the peak areas were measured with a Varian CDS 101 electronic integrator.

3. VARIATION OF PYROLYSIS PARAMETERS

In the study of the influence of the pyrolysis parameters cis-1,4-polybutadiene, PB, polystyrene, PS, poly(methyl methacrylate), PMMA, and polyacrylonitrile, PAN, were used as test substances.

3.1 The sample size

3.1.1. The temperature-time profile of the sample

The most important parameter in pyrolysis is the temperature of the sample. It determines the rates at which the pyrolysis

products are formed. Due to the low heat conductivity of most samples, it will vary across the thickness of the sample. As the temperature of the sample is difficult to measure, the pyrolysis temperature is commonly defined as the temperature of the pyrolyzer. A study of a model substance was therefore made in order to illustrate the effect of the error caused by the common temperature definition, paper I. The temperature of the sample was measured indirectly from the rate of degradation of cis-1,4-polybutadiene.

An equation was derived for the heating of a sample placed on a pyrolyzer with a known temperature. The derivation, started from Newton's law of cooling. Equations (1) and (2) give the average temperature of the sample as a function of the heating time, $T_s(t)$. It was assumed that the heating of the pyrolyzer consisted of a linear temperature rise, followed by a period at constant temperature.

During the temperature rise time:

$$T_s(t) = T_0 + \frac{k_{in} \cdot r \cdot t}{(k_{in} + k_{out})} - \frac{k_{in} \cdot r}{(k_{in} + k_{out})^2} \cdot \{1 - \exp[-t \cdot (k_{in} + k_{out})]\} \quad (1)$$

During the following period of constant temperature of the pyrolyzer

$$T_s(t) = \frac{k_{in} \cdot T' - k_{out} \cdot D}{k_{in}} + (T'_s - \frac{k_{in} \cdot T' - k_{out} \cdot D}{k_{in}}) \cdot \exp[-k_{in} \cdot (t - TRT)] \quad (2)$$

where k_{in} and k_{out} are reciprocal time constants for the heat flow in and out of the sample. T_0 is the initial temperature of the pyrolyzer and a thin sample slab close to the foil, TRT is the temperature rise time, and r is the heating rate of the pyrolyzer. T'_p and T'_s are the temperatures of the pyrolyzer and sample respectively when $t = TRT$. D is the temperatures difference between the sample and the carrier gas passing immediately over the surface.

The parameters which are characteristic for each sample are k_{in} and k_{out} . The value of D is dependent on the heat capacity and the flow rate of the carrier gas.

To determine the value of the most important parameter, viz k_{in} , the rate of degradation of cis-1,4-polybutadiene was studied. The relation between the rate constant, k , and the pyrolysis temperature, t , was obtained from determination of E_a and A in the Arrhenius' equation, $k = A \cdot e^{-E_a/RT}$ by pyrolysis of a constant sample size at different temperatures.

The values of the rate constant for samples of varying thicknesses sequentially pyrolyzed [12] at a constant temperature (500°C) were also measured. A fitting was made to k' in equation (3)

$$\frac{1}{t} \int_0^t A \cdot e^{-E_z/RT_s(t)} dt = k' \quad (3)$$

by varying k_{in} . The newtonian heat transfer coefficient k_{in}

was found to be $4 \cdot 10^{-3} \text{ cal cm}^{-2} \text{ k}^{-1} \text{ s}^{-1}$ for the transfer of heat from the pyrolyzer to the polymer. The corresponding heating profiles were calculated for some sample thicknesses, fig. 6, paper I.

The property of polybutadiene to be degraded only to a very limited extent at low temperatures was utilized to carry out the investigation. The sample size could be regarded constant during a sequence of consecutive pyrolyses.

An interesting observation was made for thin samples ($< 0.5 \mu\text{m}$). The rate constants increased more than expected with decreasing sample thickness. At the same time a lower monomer yield was obtained figs. 2 and 4, paper I. The phenomena were ascribed to the catalytic activity of platinum. If samples of 5-10 μg , 1-2 μm thickness, are used there is still a relatively quick heating of the sample and the effect of catalysis from platinum should be negligible.

In an experiment, preliminary to paper I, a mixture of PB and PMMA was pyrolyzed. PB was first applied to the foil in varying thicknesses, 0-2 μm . Thereafter a constant amount of PMMA was added to give a layer over the PB. Thus PB was used as a model spacer and the degradation of PMMA was used to measure the temperature. As PMMA is degraded at a lower temperature than PMMA, a pyrolysis temperature of 490°C was used. The PB was

degraded less than in the experiments of paper I. The value $6 \cdot 10^{-3} \text{ cal cm}^{-2} \text{ K}^{-1} \text{ s}^{-1}$ was obtained for the heat transfer coefficient. As PMMA does not give a limiting yield but is degraded completely, the results were not affected by the temperature gradient, in contrast to the case reported in fig. 2, paper I. Nor was there any increase of the rate of degradation of PMMA at low thicknesses, as a layer of PB prevented direct contact with the metal which might catalyze the reaction.

3.1.2 Detection limits

The effect of low monomer yield from a thin sample, noted in paper I was further studied in paper II, not only for PB but also for PS and PMMA. This investigation was also made with a platinum foil in the pyrolyzer.

Low yields affect mainly the detection limits. Thence the experiments were focussed on a determination of the detection limits. It was found that 1 ng of PS, 10 ng of PB and 100 ng of PMMA could be detected with a flame ionization detector. These amounts correspond to 0.2, 2 and 20 nm average thickness respectively. At least 0.2 nm is less than a monolayer of polymer over the surface where the solution had been applied.

To reduce the catalytic effect of the foil, a dilute sample solution was added together with a known amount of another polymer. The added polymer should not give pyrolysis products with the same retention time as the examined monomer.

Nevertheless the addition increased the yield of monomer. The detection limits were moved downwards with about one decade.

It is well known that adsorption of the sample passing through a chromatographic column can occur [13,14]. The low yields from the thin samples pyrolyzed could thus be caused by adsorption effects. However, adsorption also implies that the retention time increases with decreasing sample size [13,14]. No such variation could be detected in the present experiments. Therefore the adsorption effects were considered negligible.

3.1.3 Quantitative analysis of large samples

When insoluble samples are to be pyrolyzed, large amounts of sample have to be used as it is impossible to prepare and mount a very thin slice of material on the foil. The reliability of quantitative determination will also be dependent on a reliable weighing of very light fragments. Thus pyrolysis sometimes has to be made with samples of 100-1000 μg . In paper II it is shown that unambiguous calibration graphs could be obtained for samples of 10-1500 μg . The highest monomer yields were obtained if the sample was pyrolyzed repeatedly with a short pyrolysis time. The relative yield (=yield per unit weight) decreased with increasing sample thickness. This decrease was shown to be caused by the lower mean temperature of the thicker sample.

The method with repeated pyrolyses is to be preferred when the main components of a sample are to be determined. If components of minor concentration are looked for, as in paper IV, a continuous pyrolysis lasting long enough for a complete pyrolysis will be advantageous. If a small yield of a pyrolysis product is divided into several portions the uncertainty of integrator registrations might increase. The calibration curve has to be made with standards pyrolyzed in the same way as the sample.

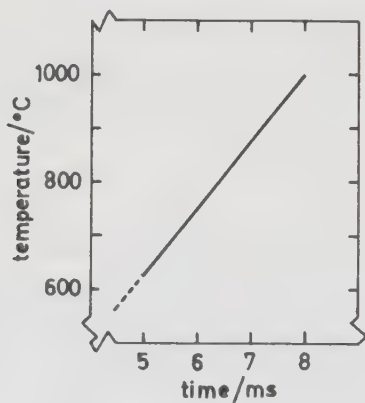
3.2 Different metals as pyrolysis filament

Very little attention has been paid to the catalytic effects of the pyrolyzer foil. In most cases where the possibility of catalysis has been examined, the effect has been assumed to be negligible, see references of paper III.

In the work described in paper III, PS, PB, PMMA, and PAN were pyrolyzed on filaments made from iron, nickel and platinum. Iron and nickel are used in Curie point pyrolyzers, either as the pure metals or as components of ferromagnetic alloys. Platinum is most commonly used for filament pyrolyzers.

With the foil pulse pyrolyzer [2] the material of the pyrolysis foil can be varied, while the remaining pyrolysis parameters are kept unchanged. Thus it should be possible to isolate the influence from the material of the filament.

The temperature-time profile of the pyrolyzers was a steep, linear temperature increase. The amplitude of the first current pulse was adjusted so that a temperature of 1000°C was reached in 8 ms. If the pulse was interrupted at 7, 6 or 5 ms the end temperature became 875, 750 and 625°C resp, see fig.



This heating program should provide information

- at the low temperatures, about the primary formation of pyrolysis products
- at the high temperatures, about the secondary degradation of primarily formed products.

The sample lags behind the temperature of the pyrolyzer, but it will be degraded at successively higher temperatures.

The results of the pyrolyses were that the same products were formed, independent of the underneath metal layer. Different metals resulted in varying yields of pyrolysis products. For the used test substances the effects of the metals could be summarized as:

The primary degradation: The yield of the main product, the monomer, was relatively independent of the type of metal, provided the sample thickness was at least 1 μm and that the pyrolysis temperature was moderate. Differences were obtained with small samples, ca 0.1 μm . The thin sample, implying a great part of the sample in direct contact with the metal, enhances the influence of the metal. High levels of monomer yields were obtained with iron, low with platinum. The formation of large fragments such as dimers and trimers was favoured by iron, retarded by platinum.

The secondary degradation, which shows up as increased yields of light fragments formed by degradation of primarily formed products, was greatest on nickel. Iron, nickel and platinum are all known to be active as hydrogenation and dehydrogenation catalysts. Either the polymers or the pyrolysis fragments could be dehydrogenated. For hydrogenation reactions a hydrogen source is needed. This could be a dehydrogenation reaction. It was observed that platinum increased the yield of hydrogenated products.

The carbonization, degradation into carbon and hydrogen, is seen as a lowered total yield of products. Platinum gave low total yields even at low temperatures. The variation of the total yields with temperature was small, which indicates that carbonization could be a primary reaction on platinum.

On nickel the total yields decreased rapidly with increasing temperature. This indicates that on nickel carbonization is mainly a secondary degradation of primarily formed products.

The order of the metals concerning their catalytic effect on the pyrolysis results was $Pt > Ni > Fe$. The differences caused by the metals were seen mainly for products with low yields. The relative yields of the main products were not much altered. The pyrolysis temperature did affect the yields much more.

When making comparisons of results obtained with different pyrolyzers the possible effect of the pyrolyzer material should be taken into consideration. This is of course especially the case when comparing results from filament pyrolyzers and Curie point types. But also when e.g. the temperature dependence of a degradation is studied with a Curie point pyrolyzer, the fact should be noted, that different temperatures are obtained with different metal materials.

In a pre-study for paper III, PB was pyrolyzed on iron, nickel and an alloy, Fe/Ni (64/36), for 2 s at temperatures varying from 600 to 1200°C. It was found that the yield was greatest on iron, somewhat lower on the alloy and least on nickel. This indicates that the metal influences the result also when it is a component of an alloy.

4. PYROLYSIS GAS CHROMATOGRAPHY APPLIED TO THE ANALYSIS OF SULFUR LINKAGES IN VULCANIZED RUBBER

Paper IV describes the application of pyrolysis gas chromatography to a difficult analytical problem.

The sulfur content of vulcanized rubber is about 1% (w/w). The vulcanization reaction will produce a number of sulfur-containing compounds. Very little is known about the reactions. The various compounds are present at low concentration which makes the studies more difficult.

A sulfur selective flame photometric detector was utilized in order to diminish the detector signal from hydrocarbons. As vulcanized rubber is an insoluble material the samples were cut and weighed before they were placed on the pyrolyzer. Samples of 40 μg could be weighed and pyrolyzed reproducibly.

The main sulfurous pyrolysis products were identified to be CS_2 , thiophene and the mono-methyl thiophenes. None of these products has been reported earlier in the literature. In contrast to earlier results, of the polymer mixtures in paper II pyrolysis reaction products were formed from a mixture of sulfur and rubber. The products were the same as from the vulcanizates, though the yields were lower. The products H_2S , CH_3SH , allyl-mercaptane, which have been reported as possible pyrolysis fragments [15], were produced only in low yields.

There was a significant difference between pyrograms of samples containing mainly polysulfidic crosslinkings and samples rich in mono- and disulfidic crosslinkings, see fig. 1, paper IV. Variation of the pyrolysis temperature indicated that the yield of volatile sulfurous compounds increased by secondary reactions, see fig. 2, paper IV. Samples vulcanized for different times produced different pyrograms. The differences were significantly larger than the variations between replicate pyrograms of the same type of material. The yield of CS_2 produced at low pyrolysis temperature could be ascribed to the disulfidic links. At high temperatures CS_2 is also produced from reactions of polysulfidic links. The methyl-tiophenes could be related to the cyclic mono-sulfides of the polymer chain.

Though the method is still at an early stage of development the result shows that the ability for the pyrolysis-chromatography method to solve difficult problems improves when the pyrolysis conditions are under control.

The above investigations have been made with synthetic polymer samples. Today the field of applications of analytical pyrolysis also includes biopolymers, organic geopolymers, taxonomy and forensic science [16].

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DETERMINATION OF THE TEMPERATURE–TIME PROFILE OF THE SAMPLE IN PYROLYSIS–GAS CHROMATOGRAPHY

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SUMMARY

The mean temperature–time profile in a sample has been determined in order to establish whether it is possible to equate the temperature of the pyrolyzer with that of the sample being pyrolyzed. This was done by studying the degradation of *cis*-1,4-polybutadiene by sequential pyrolysis. The rate of degradation was determined for different amounts (0.5–20 μg) of sample. The temperature dependence of the degradation rate was determined from an Arrhenius plot. The experimental results were combined with theoretically derived expressions for the heating of samples subjected to pyrolysis. The temperature–time profiles of different amounts of sample could then be calculated.

It was found that samples thinner than 1 μm were heated to a mean temperature of 95% of the temperature of the pyrolyzer in 40 ms or faster. Too thin samples can give rise to noticeable catalytic effects.

By choosing the appropriate pyrolysis conditions of sample thickness, time and temperature it is possible to assume that the temperature of the sample is nearly the same as that of the pyrolyzer.

INTRODUCTION

The temperature of the sample is a key factor in pyrolysis–gas chromatography. The pyrolysis temperature is usually defined as the temperature of the pyrolyzer, which is easier to measure than the temperature of the sample. Attempts have been made to determine the “true pyrolysis temperature” (TPT), meaning the temperature reached by the sample [1,2]. For very small samples the temperature of the pyrolyzer and the sample should be essentially identical.

From measurements with thermocouples spot-welded on the filament, it was found that with a 0.05 μm thick film of sample on the filament the temperature–time profile was very close to that of the uncoated filament [2]. Barlow et al. [3] have found that the rates of thermal decomposition of poly(methyl methacrylate) and polystyrene were independent of the sample thickness for layers less than 0.02 μm thick.

The literature on analytical pyrolysis contains few calculations of the heating of the sample [4,5]. However, in studies of dynamic thermochemical methods [e.g., differential scanning calorimetry (DSC)] more comprehensive

theoretical treatments have been given [6–8]. They were initiated by the observation of discrepancies depending on the actual sample size. Unfortunately, these calculations cannot be applied directly to analytical pyrolysis, as the temperature–time profiles of the heaters differ. In DSC the temperature of the heater is gradually increased, while the temperature of the pyrolyzer is kept constant after a rapid rise to the desired temperature. This work constitutes one part of a project in which the influence of different parameters on the qualitative and quantitative results from pyrolysis–gas chromatography has been investigated [9].

The aim of this paper is to show, experimentally and theoretically, how the temperature of a sample is dependent on the sample size and the pyrolysis time.

EXPERIMENTAL

Apparatus and working conditions

The pyrolyzer consists of a thin (0.012 mm) platinum foil, 15 mm long and 2.6 mm wide, heated by two current pulses. The first pulse is 8 ms and the second can be varied from zero to several seconds. The amplitude of the pulses should be chosen so that the temperature rises to the desired level during the first pulse and is kept at that temperature during the second. In this work the second pulse was 0.050, 0.200 or 1.000 s. The pyrolysis apparatus has been described in detail in an earlier paper [9].

The pyrolysis temperature, defined as the temperature at the middle of the foil, is determined both from the change of resistance of the foil and from a calibrated photodiode. The photodiode measures the light emitted from an area of 1 mm² at the middle of the foil. The temperature calibration has been described separately [10].

The pyrolysis temperature was 500°C in all of the experiments, except when making the Arrhenius plot, when it was varied from 450 to 510°C.

The pyrolyzer was connected directly to the column in a Varian 1860 gas chromatograph. A 3 m × 1/8 in. steel column, 1.9 mm I.D., packed with 15% Apiezon L on Chromosorb W AW DMCS (80–100 mesh) was used. The column temperature was held at 150°C. The carrier gas (nitrogen) flow-rate was 17.0 ml/min. The hydrogen flow-rate for the flame-ionization detector was 17.0 ml/min and the air flow-rate was about 200 ml/min. The peak areas of the pyrograms were measured with a CDS 101 integrator. The numerical calculations were performed with an Alpha LSI-2 computer equipped with a line-printer, teletype and an X–Y recorder.

Sample preparation

Amounts of 1.0, 5.0 and 10.0 mg of *cis*-1,4-polybutadiene (Cariflex 1220, Shell Chemicals, $M_w = 520,000$) were dissolved in 2 ml of toluene. Aliquots of 1 μ l of sample solution were placed on the foil using a 1- μ l Hamilton syringe. To obtain samples of 10, 15 and 20 μ g the procedure was repeated

once, twice and three times further, respectively, with the solution containing 5.0 mg/ml. The samples spread over an area of about 6 mm² in the middle of the foil. Most of the solvent was evaporated before the pyrolyzer was placed in its chamber.

Sequential pyrolysis

The rate of degradation was studied by the sequential pyrolysis technique [11]. In this method the pulse time is so short that only a portion of the sample is degraded during each pyrolysis. The pyrolysis can thus be performed stepwise, until the amount of products formed becomes negligible.

If the degradation behaviour is known, much time can be saved if only the first few of the sequences are studied. Experimentally the first pyrograms should be the most reliable.

THEORETICAL

Calculations of the degradation rate

From a sequential pyrolysis the rate of degradation of a sample can be determined as the rate of formation of one of the pyrolysis products. For a first-order degradation reaction the integrated rate equation then becomes

$$-\ln(1 - C/C_{\text{tot}}) = \int_0^t k \, dt \quad (1)$$

where

C = the sum of integrator counts at time t for the peak studied

C_{tot} = the total sum of integrator counts after all of the pyrolyses in a sequence for the peak studied

t = the accumulated pyrolysis time (not including the temperature rise time)

In this work C_{tot} was determined by extrapolation of the first values of C . The value obtained is denoted by C_{tot}' .

If the temperature varies with the time, then

$$\int_0^t k \, dt = \int_0^t A \cdot \exp\left(-\frac{E_a}{RT(t)}\right) dt \quad (2)$$

as the rate constant, k , varies with the temperature according to

$$k = A \cdot \exp(-E_a/RT) \quad (3)$$

where A is the frequency factor, E_a the activation energy, R the gas constant and T the absolute temperature. The Arrhenius plot is obtained by determination of k according to eqn. 1 and using the logarithm of eqn. 3 for evaluation of E_a and A .

Calculation of the heating of a sample

According to Newton's law of cooling, the heat flux between two materials with different temperatures is proportional to the temperature difference between the two materials. For a sample occupying an area a , the newtonian flow of heat, J_{in} , from the pyrolyzer into the sample becomes

$$J_{in} = h_{in} \cdot a \cdot (T_p - T_s) \quad (4)$$

where h_{in} is the newtonian heat transfer coefficient, T_p is the temperature of the pyrolyzer and T_s the temperature of the sample. If the temperature within the sample is homogeneous, the newtonian flow of heat out of the opposite surface is

$$J_{out} = h_{out} \cdot a \cdot (T_s - T_{gas}) \quad (5)$$

where h_{out} is the heat transfer coefficient and T_{gas} is the temperature of the carrier gas.

The heating rate, dT_s/dt , of a sample of mass m implies a power consumption, P , determined by

$$P = C_p \cdot m \cdot \frac{dT_s}{dt} \quad (6)$$

where C_p is the specific heat capacity of the sample.

If no heat is generated in the sample, the power balance is represented by $P = J_{in} - J_{out}$, or

$$C_p \cdot m \cdot \frac{dT_s}{dt} = h_{in} \cdot a \cdot (T_p - T_s) - h_{out} \cdot a \cdot (T_s - T_{gas}) \quad (7)$$

which can be written as

$$\frac{dT_s}{dt} + (k_{in} + k_{out}) \cdot T_s = k_{in} \cdot T_p + k_{out} \cdot T_{gas} \quad (8)$$

where

$$k_{in} = \frac{h_{in} \cdot a}{C_p \cdot m}$$

and

$$k_{out} = \frac{h_{out} \cdot a}{C_p \cdot m}$$

The temperature-time profile of the pyrolyzer consists of two parts: the temperature rise time (TRT) and the period of constant temperature.

The temperature rise time

During this period the temperature of the pyrolyzer increases approximately linearly, i.e.,

$$T_p(t) = T_0 + r \cdot t \quad \text{at } t = 0, T_s = T_0 \quad (9)$$

where T_0 is the initial temperature and r the heating rate. For the moment it is also assumed that $T_{\text{gas}} = T_0$ and that it is independent of t . The solution of eqn. 8 then becomes

$$T_s(t) = T_0 + \frac{k_{\text{in}} \cdot r \cdot t}{(k_{\text{in}} + k_{\text{out}})} - \frac{k_{\text{in}} \cdot r}{(k_{\text{in}} + k_{\text{out}})^2} \cdot \{1 - \exp[-t \cdot (k_{\text{in}} + k_{\text{out}})]\} \quad (10)$$

The above expressions for the sample—pyrolyzer system are identical with those derived for the heating of a sample in a differential scanning calorimeter [12].

The period of constant temperature of the pyrolyzer

The period starts at $t = \text{TRT}$, which in this work is 8 ms. The initial temperature of the sample is denoted by T'_s and the temperature of the pyrolyzer, which is constant during this period, is denoted by T'_p . Further, it is assumed that the temperature of the carrier gas differs from that of the sample by a constant value D . With these conditions, the solution of eqn. 8 becomes

$$T_s(t) = \frac{k_{\text{in}} \cdot T'_p - k_{\text{out}} \cdot D}{k_{\text{in}}} + \left(T'_s - \frac{k_{\text{in}} \cdot T'_p - k_{\text{out}} \cdot D}{k_{\text{in}}} \right) \cdot \exp[-k_{\text{in}} \cdot (t - \text{TRT})] \quad (11)$$

Tabulated values of h_{in} and h_{out} are given in the literature [13]. They are not very precise because they depend on the physical properties of the materials, such as the roughness of the metal surface, the type of sample and the velocity and properties of the carrier gas. It is possible to determine one of the constants for the actual pyrolysis conditions by studying the pyrolysis of *cis*-1,4-polybutadiene. It is known [11] that both the total amount of pyrolysis products and the amount of monomer are proportional to the pyrolysis temperature.

The rate of pyrolysis is, of course, also dependent on the temperature according to eqn. 3. As most of the heat flow into the sample is used for increasing its temperature and only a small fraction is lost to the carrier gas and by radiation, it is reasonable to try to estimate losses and measure h_{in} . In the literature [13], h_{out} for a surface in contact with oil has been given from $1.4 \cdot 10^{-3}$ to $4 \cdot 10^{-2} \text{ cal cm}^{-2} \text{ K}^{-1} \text{ s}^{-1}$.

The range of values for h_{out} for various conditions is [13] $2.7 \cdot 10^{-5}$ to $1.1 \cdot 10^{-3} \text{ cal cm}^{-2} \text{ K}^{-1} \text{ s}^{-1}$, and for a polished surface in still air at small temperature differences $1.8 \cdot 10^{-4}$ to $2.3 \cdot 10^{-4}$. The carrier gas moves over the foil with a linear velocity of ca. 0.7 cm s^{-1} ; it has passed over a 7 mm length of foil when it comes to the sample position. The foil temperature increases gradually towards the sample site. Thus, the carrier gas is heated before, and possibly also when, passing over the sample. If the temperature of the carrier gas differs only slightly from that of the sample, the flow of heat out of the sample becomes negligible, which means that the value $h_{\text{out}} = 0$ can be chosen (see eqn. 5).

An estimation of the transmission of heat out of the sample can be made with the Stefan—Boltzmann law. Information is available about transmission through thin oil films on metal surfaces [13]. For the sample thickness used

in this work, at most $3\text{ }\mu\text{m}$, the emissivity is almost identical with that of the uncovered metal. Using an emissivity of 0.1, the radiation loss from the platinum was found to be $0.05\text{ cal cm}^{-2}\text{ s}^{-1}$ at 500°C ; only a small fraction of this should be emitted from the sample. The absorption by the sample should also be of the same size. It is therefore possible to neglect the radiative heat transfer in the calculations.

Determination of h_{in}

The constants E_a and A can be determined (see eqn. 3) from measurements over a larger temperature interval. The rate constant can be determined by using measured amounts of pyrolysis products produced as a function of time at a fixed temperature (see eqn. 1). It can also be calculated (cf. eqn. 3) from

$$k' = \frac{1}{t_1} \int_0^{t_1} A \cdot \exp[-E_a/RT_s(t)] dt \quad (12)$$

where $T_s(t)$ is calculated from eqns. 10 and 11 using an estimated value of h_{in} . This is repeated for various h_{in} values until k' is equal to the constant obtained from eqn. 1. The procedure was repeated for different sample sizes until a value of h_{in} was found which on the average gave the best fit.

RESULTS

Sequential pyrolyses were run and the degradation rate was calculated for each amount of sample (0.5, 2.5, 5, 10, 15 and $20\text{ }\mu\text{g}$) and for each pyrolysis time (0.050, 0.200 and 1.000 s). Fig. 1a shows the pyrogram of a sample sequentially pyrolyzed. In Fig. 1b the pyrogram of the remainder of the sample pyrolyzed at 1000°C for 0.2 s is shown. The natural logarithm of the degradation rate was plotted versus the amount of sample at the three different pyrolysis times used (see Fig. 2).

An Arrhenius plot (see eqn. 3) was made with $5\text{ }\mu\text{g}$ of polybutadiene pyrolyzed at different temperatures of the platinum foil (see Fig. 3). The line, obtained by linear regression, gave an activation energy of $176 \pm 8\text{ kJ mole}^{-1}$ and a frequency factor of $A = \exp(28.5 \pm 1.3)\text{ s}^{-1}$.

In Fig. 4 the yield, defined as the integrator counts, C_{tot}' , per microgram of sample, is plotted against the different sample sizes for the three different pyrolysis times used in the sequential pyrolyses.

The heat transfer coefficient, h_{in} , can now be determined as E_a and A are available from Fig. 3. The area, a , covered by the samples was approximately 0.06 cm^2 . The specific heat of melted polybutadiene was estimated to be $C_p = 0.5\text{ cal g}^{-1}\text{ K}^{-1}$ from the values given for other liquid hydrocarbons [14]. The temperature-time profile of the pyrolyzer consisted of an 8-ms linear increase from 108 to 500°C and a period of constant temperature at 500°C . Owing to the mathematical complexity of eqn. 12, the integration was made numerically using the trapezoidal rule.

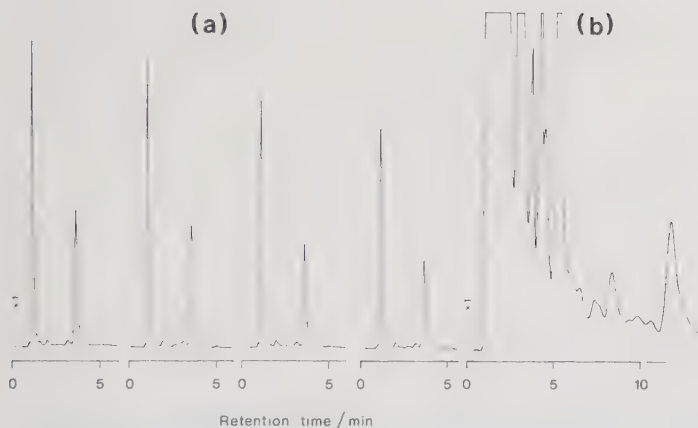


Fig. 1. *cis*-1,4-Polybutadiene ($5\text{ }\mu\text{g}$) pyrolyzed (a) four times at 500°C for 0.050 s and (b) once at 1000°C for 0.200 s .

With these conditions, h_{in} was estimated to be $4 \cdot 10^{-3}\text{ cal cm}^{-2}\text{ K}^{-1}\text{ s}^{-1}$, for $h_{\text{out}} = 0$, from fitting mainly to the 0.2-s pyrolyses. This falls within the interval given in the literature [13] for a surface in contact with oil, viz., $1.4 \cdot 10^{-3}$ to $4 \cdot 10^{-2}\text{ cal cm}^{-2}\text{ K}^{-1}\text{ s}^{-1}$.

In Fig. 5 $\ln k'$ versus the sample size is shown for $h_{\text{in}} = 4 \cdot 10^{-3}\text{ cal cm}^{-2}\text{ K}^{-1}\text{ s}^{-1}$ and pyrolysis times of 0.050 , 0.200 and 1.000 s . If $h_{\text{out}} = 1.1 \cdot 10^{-3}\text{ cal cm}^{-2}\text{ K}^{-1}\text{ s}^{-1}$ and the temperature difference between the sample and the carrier gas is 10°C , the values of $\ln k'$ will be 0.1 unit lower. The shape of the curves will not be changed significantly.

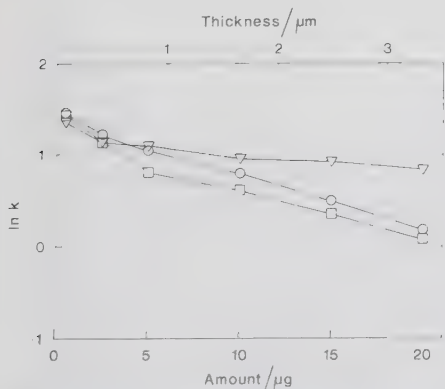


Fig. 2. Natural logarithm of the experimentally found rate constant plotted against the amount of *cis*-1,4-polybutadiene and the corresponding estimated thickness for pyrolysis times of 1.000 s (∇), 0.200 s ($\circ$) and 0.050 s ($\square$) in sequential pyrolysis.

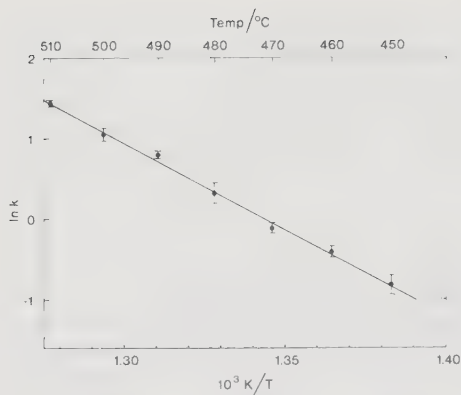


Fig. 3. Arrhenius plot of the rate of degradation of 5 μg of *cis*-1,4-polybutadiene when sequentially pyrolyzed at temperatures between 450 and 510°C with a pyrolysis time of 0.200 s. The intervals marked are the standard deviations for each temperature.

With the value of h_{in} determined, the temperature—time profile of the sample could be calculated, which was the aim of the work. In Fig. 6 the value of h_{in} found in Fig. 5 was used to obtain the time dependence of the average temperature of the different amounts of sample (0.5, 2.5, 5, 10, 15 and 20 μg), $h_{\text{out}} = 0$. It can be seen that the curve for the 0.5- μg sample (ca. 0.1 μm) essentially coincides with that of the pyrolyzer. The temperature of the 5- μg sample (ca. 1 μm) reached 95% of the temperature of the pyrolyzer after 40 ms.

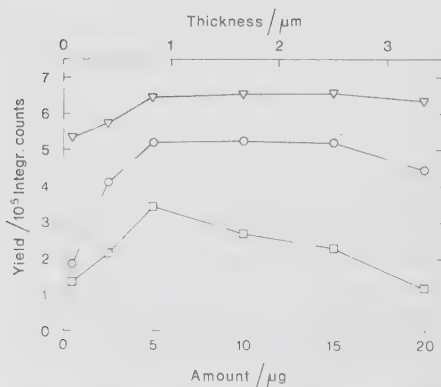


Fig. 4. Yield of butadiene obtained per microgram of sample plotted against the amount of sample when different amounts of sample were sequentially pyrolyzed with different pyrolysis times: 1.000 s (∇), 0.200 s ($\circ$) and 0.050 s ($\square$).

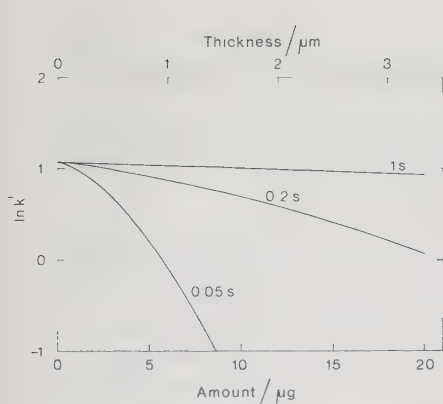


Fig. 5. Natural logarithm of the calculated value of the rate constant plotted against the sample size for $h_{in} = 4 \cdot 10^{-3}$ and $h_{out} = 0 \text{ cal cm}^{-2} \text{ K}^{-1} \text{ s}^{-1}$.

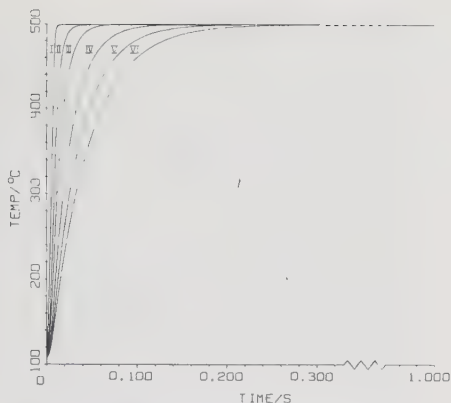


Fig. 6. Calculated temperature-time profiles for different values of k_{in} : (I) 960; (II) 192; (III) 96; (IV) 48; (V) 32; and (VI) 24 s^{-1} . In the present system these correspond to 0.5, 2.5, 5.0, 10.0, 15.0 and $20.0 \mu\text{g}$ of sample.

DISCUSSION

The results in Fig. 2 show that the degradation rate is higher for small amounts and longer pyrolysis times used. This means that the average temperature in a thinner sample is higher than in a thicker sample. If a sample is pyrolyzed for a long time, the temperature has time to reach a higher value.

However, from Fig. 4 it is clear that at sample sizes lower than $5 \mu\text{g}$, the yield is lower than expected from Fig. 2. The explanation is probably that at low sample sizes the catalysis becomes relatively more important. The degradation rate is influenced and side-reactions, which produce carbon and hydrogen as end products [11], become dominating. It is evident that for the longest pyrolysis time and for relatively large amounts of sample ($> 5 \mu\text{g}$) the yield is nearly constant. This indicates that the sample temperature is homogeneous during the main part of the pyrolysis. At shorter pyrolysis times the yield decreases much more when increasing the sample size.

When comparing $\ln k$ and $\ln k'$ in Figs. 2 and 5 it can be noted that for small samples ($< 5 \mu\text{g}$) and the two longer pyrolysis times the variation of $\ln k'$ with the sample size is moderate whereas there is a relatively steep increase in $\ln k$. This supports the assumption made earlier that the smaller the sample size the more noticeable becomes the catalytic effect of the metal foil, which causes increased reaction rates.

Over the whole sample interval shown, the curves for the 0.2- and 1.0-s pyrolyses are very similar in Figs. 2 and 5. A large discrepancy is seen, however, for the pyrolyses of 0.050 s. The reason for this is that the model used for calculating the values in Fig. 5 does not take the temperature gradient in

the sample into consideration; it is assumed that the temperature is homogeneous. According to Fig. 5, which depends on the model, no observable degradation should take place in samples larger than $10\text{ }\mu\text{g}$. In Figs. 2 and 4, which depend only on the direct measurement of the amount of pyrolysis product, degradation is observed even for the largest sample sizes. Owing to the temperature gradient in the sample, the part of the sample next to the pyrolyzer will always be subjected to pyrolysis.

The temperature gradient of the sample is dependent on the conduction of heat and the convection within the sample. To obtain an estimate of the influence of the temperature gradient, it was assumed that the temperature gradient in the sample was linear.

With this condition, rough calculations have shown that the difference between $\ln k$ and $\ln k'$ for the 0.050-s pyrolyses is considerably reduced.

For the longer pyrolysis times the effect of the temperature gradient does not affect the value of $\ln k'$ appreciably. The calculations also gave expected values of the yield near the experimentally found values, so the temperature gradient is one reason for the distance between the three curves in Fig. 4, another being the effect of catalysis.

The model used in this paper is, of course, idealized in several ways. It has been assumed that no heat of reaction is involved in the pyrolysis reaction. As the value of h_{in} obtained was found from the experiments it includes the effect of the heat consumption due to this reaction. The temperature-time profile of the foil is more curved than the linear-constant type assumed here [9]. The temperature of the foil in the sample area is not completely homogeneous [9]. It is also difficult to apply all samples to spots with exactly the same temperature profile. The model used for the calculation is certainly indirect. There is a systematic error, although from the experiments it can be concluded that it is small, in the determination of E_a and A in the Arrhenius plot because, from one point of view, a very small sample should be used in order to have equality between the sample and the foil temperatures. From another point of view, the sample size should be so large that catalytic effects are negligible.

Barlow et al. [3] concluded that the sample thickness should be at most $0.02\text{ }\mu\text{m}$, which corresponds to a sample size of $0.1\text{ }\mu\text{g}$ on our foil. Their measurements were confined to a range that corresponds to the very early part of Fig. 2. The downward trend in this range has been explained by catalysis in this work. Wolf et al. [2], who spot-welded thermocouples to the filament and determined the time-temperature profile for various sample sizes, concluded that the thickness should be less than $0.05\text{ }\mu\text{m}$. Their experimental conditions were, however, very different from those used in this investigation.

CONCLUSIONS

As the pyrolysis temperature is defined as the temperature of the pyrolyzer, the temperature of the sample should be as near to that of the pyrolyzer as possible. From the results, it can be concluded that, provided the

pyrolysis time is long enough, it is possible to use relatively thick samples for pyrolysis. The temperature of the sample is the same as that of the pyrolyzer during the main part of the pyrolysis.

From the present experiments it can also be concluded that, although the temperature of the sample quickly becomes homogeneous, too thin samples ($<0.5 \mu\text{m}$) could give erroneous results because of a proportionately greater influence of catalysis from the pyrolyzer.

ACKNOWLEDGEMENT

The authors thank Professor Gillis Johansson for valuable discussions.

LIST OF SYMBOLS

Symbol	Dimensions		Definition
	Units used in this paper	SI units	
A	s^{-1}	s^{-1}	frequency factor
a	cm^2	m^2	area
C	—	—	integrator counts
C_{tot}	—	—	integrator counts (total)
C'_{tot}	—	—	calculated C_{tot}
C_p	$\text{cal g}^{-1} \text{K}^{-1}$	$\text{J kg}^{-1} \text{K}^{-1}$	specific heat capacity
D	$^{\circ}\text{C}$ or K	$^{\circ}\text{C}$ or K	$T_s - T_{\text{gas}}$
E_a	cal mole^{-1}	J mol^{-1}	activation energy
$h_{\text{in}}, h_{\text{out}}$	$\text{cal s}^{-1} \text{K}^{-1} \text{cm}^{-2}$	$\text{W K}^{-1} \text{m}^{-2}$	heat transfer coefficients
$J_{\text{in}}, J_{\text{out}}$	cal s^{-1}	W	newtonian heat flux
k	s^{-1}	s^{-1}	experimentally found rate constant
k'	s^{-1}	s^{-1}	calculated rate constant
$k_{\text{in}}, k_{\text{out}}$	s^{-1}	s^{-1}	$k_{\text{in}} = h_{\text{in}}a/C_p m$, $k_{\text{out}} = h_{\text{out}}a/C_p m$
m	g	kg	mass of the sample
P	cal s^{-1}	W	power
R	$\text{cal mole}^{-1} \text{K}^{-1}$	$\text{J mol}^{-1} \text{K}^{-1}$	gas constant
r	$^{\circ}\text{C s}^{-1}$	K s^{-1}	heating rate
T	$^{\circ}\text{C}$ or K	$^{\circ}\text{C}$ or K	temperature
T_{gas}	$^{\circ}\text{C}$ or K	$^{\circ}\text{C}$ or K	temperature of the carrier gas
T_0	$^{\circ}\text{C}$ or K	$^{\circ}\text{C}$ or K	temperature at $t = 0$
T_p	$^{\circ}\text{C}$ or K	$^{\circ}\text{C}$ or K	temperature of the pyrolyzer
T_p^r	$^{\circ}\text{C}$ or K	$^{\circ}\text{C}$ or K	pyrolysis temperature
T_s	$^{\circ}\text{C}$ or K	$^{\circ}\text{C}$ or K	temperature of the sample
T_s^r	$^{\circ}\text{C}$ or K	$^{\circ}\text{C}$ or K	temperature of the sample at the end of the temperature rise time of the pyrolyzer
t	s	s	time
TRT	s	s	temperature rise time

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SAMPLES FROM ng TO mg IN PYROLYSIS—GAS CHROMATOGRAPHY *

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SUMMARY

Samples of polystyrene⁻, polybutadiene and poly(methyl methacrylate) were pyrolysed in amounts from nanograms to milligrams. With a gas chromatograph equipped with a flame-ionization detector it was possible to detect 1 ng of polystyrene, 10 ng of polybutadiene and 100 ng of poly(methyl methacrylate).

After the addition of microgram amounts of another substance the yield of the pyrolysis products from the smallest samples increased.

Amounts from micrograms to milligrams were pyrolysed and unambiguous calibration graphs were obtained. The highest yields were obtained by pyrolysing repeatedly for relatively short periods until no further products were formed.

INTRODUCTION

Among the parameters that need to be defined for comparable and reproducible pyrolysis results, the sample size is one of the most important [1–5]. The main reason is that the temperature of the sample is closely related to the sample size. Hence, Barlow et al. recommended the use of very small sample sizes (nanograms), as small samples would be heated almost as quickly as the pyrolyser [6].

Another reason for the importance of the sample size is its influence on secondary reactions. Schmid and co-workers used 1 μ g or less to avoid recombination reactions yielding less characteristic pyrograms [7,8]. Jones and Reynolds [2] obtained more complex pyrograms for smaller samples (picograms). In earlier work we found that the yield of butadiene obtained per microgram of polybutadiene pyrolysed decreased for sample sizes of less than 5 μ g [9]. From that investigation it could also be concluded that sample sizes up to 20 μ g were heated sufficiently fast for most purposes.

In practical work, microgram amounts of sample are most often pyrolysed, although there are occasions when extremely small (nanograms) or very large (milligrams) amounts have to be used. The former can occur with dilute solutions. Large amounts of sample might have to be used for the pyrolysis

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of insoluble samples. Trojer and Ericsson showed that it was possible to pyrolyse vulcanized rubber samples from 40 to 360 μg reproducibly [10]. In the analysis of microorganisms larger amounts of samples also have been used, although the reproducibility has not always been good.

The aim of this paper is to show how the yield of the volatile pyrolysis products is influenced by the sample size. We show how to improve the pyrolysis results with nanogram amounts of sample and the pyrolysis conditions to be chosen in order to increase the yield when pyrolysing milligram amounts of sample.

EXPERIMENTAL

Apparatus and operating conditions

The pyrolyser consisted of a thin (0.012 mm) platinum foil, 15 mm long and 2.6 mm wide. For large solid samples it was necessary to form a cavity of 2.5 mm I.D. where the samples were placed in the foil, otherwise they tended to fall off. The pyrolyser was heated by two current pulses. The first, which was for 8 ms, increased the temperature of the pyrolyser to the desired pyrolysis temperature. The second, the length of which could be varied, kept the pyrolyser at that temperature. With the ordinary pyrolysis foil there was a temperature decrease followed by an overshoot at the beginning of the second pulse; both were less than 10°C . With the modified pyrolyser the temperature decreased by ca. 100°C after the temperature rise time. The pyrolysis temperature was reached again after about 0.5 s. The temperature of the pyrolysis chamber was 115°C . The pyrolysis apparatus has been described in detail in an earlier paper [5].

The pyrolysis temperature, defined as the temperature at the middle of the foil, was determined with a calibrated photodiode and from the resistance of the foil. The temperature calibration has been described earlier [11].

The pyrolyser was connected directly to the column in a Varian 1860 gas chromatograph. A 2 m $\times$ 1/8 in. O.D., 1.9 mm I.D., steel column, packed with 15% Apiezon L on Chromosorb W AW DMCS (80–100 mesh) was used. The carrier gas (nitrogen) flow-rate was 20.0 ml/min. The hydrogen flow-rate for the flame-ionization detector was 20.0 ml/min and the air flow-rate was 240 ml/min. The peak areas of the pyrograms were measured with a CDS 101 integrator. The pyrolysis conditions are shown in Table 1.

The range of the flame-ionization detector used was normally 10^{-11} A. For the smallest samples 10^{-12} A had to be used, and 10^{-9} A for the investigation of the large samples.

Sample preparation

The substances used in this study were *cis*-1,4-polybutadiene (Cariflex 1220, Shell Chemicals, Berre, France, $M_w = 520,000$), polystyrene (technical product, Swedish Polystyrene Factory Ltd., Kävlinge, Sweden, $M_w = 260,000$) and poly(methyl methacrylate) (bead polymer, Polysciences Inc.,

TABLE 1
Pyrolysis conditions

Polymer	ng- μ g		μ g-mg	
	Time (s)	Temperature (°C)	Time (s) *	Temperature (°C)
Polystyrene	1	565	2	800
Polybutadiene	2	500	1	1000
Poly (methyl methacrylate)	2	470	1	700

* The pyrolysis was repeated until the sample was consumed and no further products were formed.

Warrington, PA, U.S.A., low molecular weight). The small amounts of sample ($\leq 20 \mu\text{g}$) were applied on the foil as $1 \mu\text{l}$ of a toluene solution prepared to give a suitable concentration of the polymer. A $1\text{-}\mu\text{l}$ Hamilton microsyringe was used and the sample was spread over an area of ca. 6 mm^2 .

The larger amounts of polystyrene and poly(methyl methacrylate) were obtained by preparing toluene solutions of the polymers in bowls. When the solvent had evaporated, polymer layers of varying thickness remained. These samples were cut so that their areas were suitable for the dimensions of the cavity in the foil. The samples were weighed on a micro-balance.

To make the polystyrene samples adhere better to the pyrolyser the foil with the sample on it was carefully heated until the polystyrene melted slightly. The poly(methyl methacrylate) samples, being more heat sensitive, were placed in the cavity, which had previously been loaded with $1 \mu\text{l}$ of toluene. The sample partly dissolved and acted as its own adhesive when the solvent evaporated. The polybutadiene was cut and weighed and, as it was a soft and sticky substance, it stuck well to the metal without any special procedure.

As the samples were restricted to a limited area, variation of the amount of sample is almost equivalent to variation of the sample thickness.

RESULTS AND DISCUSSION

Pyrolysis of ng- μ g samples

Polystyrene

Various amounts (from 1 ng to $20 \mu\text{g}$) of polystyrene were pyrolysed at 565°C for 1 s . At this low temperature the effect of catalysis should be relatively small, whereas the yield of styrene is almost maximal [12]. Typical pyrograms are shown in Fig. 1. The main product was the monomer, styrene, which constituted at least 98% of the total yield detected. The area of the styrene peak was plotted logarithmically versus the amount of polystyrene pyrolysed (curve 1 in Fig. 2). It was possible to detect 1 ng , although the standard deviation was large, as shown, being ca. 60% for both 1 ng and 10 ng .

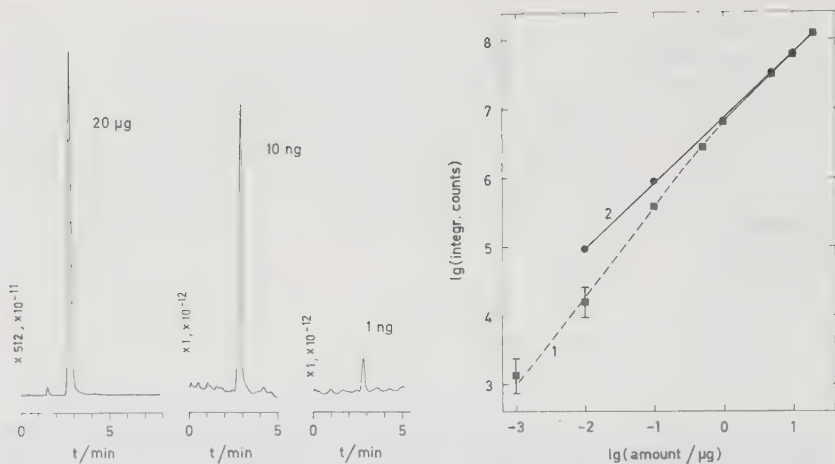


Fig 1. Pyrograms of polystyrene pyrolysed for 1 s at 565°C. The main product in each instance was styrene. Column temperature: 150°C.

Fig 2. Curve 1: yield of styrene formed versus amount of polystyrene pyrolysed. Curve 2: calibration graph for polystyrene pyrolysed together with 5 µg of polybutadiene. The standard deviations are marked where they are larger than the symbols used.

In the pyrolysis of polymer samples the standard deviation is typically better than 1%, which was also the case between 1 and 20 µg. In ref. 14 it has been shown that the metal surface could affect the reactions, which would decrease the yield obtained from the small samples. To reduce this effect, the polystyrene samples were also pyrolysed together with 5 µg of polybutadiene, both having been dissolved together. The area of the styrene peak from these runs is also plotted in Fig. 2 (curve 2). The pyrolysed polybutadiene gave rise to a small peak of about the same size as 10 ng of polystyrene in these experiments and with the same retention time as styrene, for which the values in the figure have been corrected. Owing to these unresolved peaks, amounts of polystyrene less than 10 ng could not be determined. The improvement achieved by the addition of the polybutadiene can be seen in Fig. 2. The increase in the yields implies that the linear part of the calibration graph was extended. Further, the reproducibility was significantly improved, as shown by the standard deviation indicated. With better separation it would probably be possible to detect 1 ng of polystyrene in 5 µg of polybutadiene.

A calibration graph was also constructed for pure polystyrene at 700°C, which is the temperature at which the yield of styrene is maximal [12]. The result was similar to that at 565°C with about the same standard deviation. The yields of the smaller samples were lower, however. This indicates that the effect of catalysis is higher at higher temperatures.

Polybutadiene

Different amounts of polybutadiene were pyrolysed for 2 s at 500°C. At

this relatively low temperature the influence of catalysis by the hot metal surface should be small. Although the conditions do not give maximal yield of monomer in the microgram range, it has been shown possible to use similar conditions for reproducible pyrolysis [13]. Typical pyrograms are shown in Fig. 3. Butadiene is the main product.

The area of the butadiene peak was plotted logarithmically versus the amount of polybutadiene pyrolysed (curve 1 in Fig. 4). The calibration graph was linear from 5 to 20 μg . The detection limit was 10 ng of polybutadiene with a standard deviation of ca. 50%. The pyrolysis of polybutadiene has earlier been shown to be sensitive to catalysis [9,14]. To reduce this effect, the polybutadiene was pyrolysed together with polystyrene, which was added to the sample solutions so that 1 μl also contained 5 μg of polystyrene. As shown in Fig. 4 (curve 2), this increased the yield of butadiene so that the calibration graph was linear over four decades. The detection limit was lowered to 1 ng, where the standard deviation was 13%. The values were corrected for the small contribution of a peak from the polystyrene, the size of which was about the same as that of 1 ng of polybutadiene.

A calibration graph was also constructed with different amounts of polybutadiene pyrolysed for 8 ms at 1000°C. At this temperature the yield of butadiene from samples in the microgram range is maximal [13], but the calibration graph deviated at amounts of 0.1 μg and less and also 10 μg and more. It was possible, however, to detect 1 ng of polybutadiene with an uncertainty of ca. 20% in the values. Consequently, in this instance the catalytic effect at high temperatures was lower than at the lower temperatures with

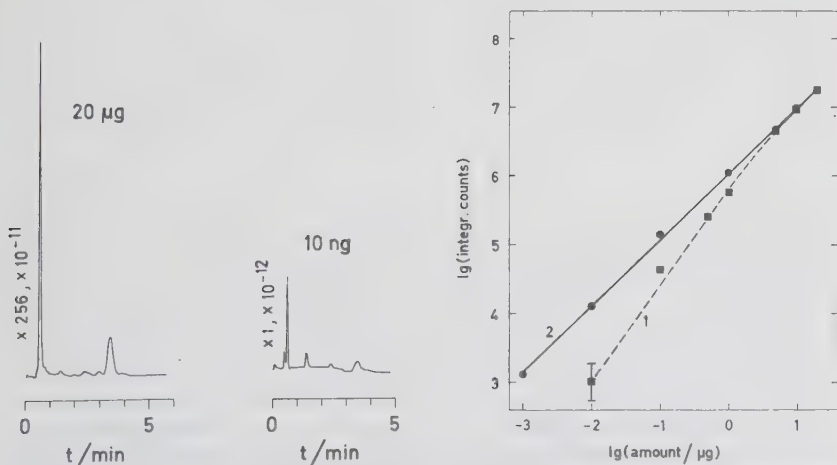


Fig. 3. Pyrograms of polybutadiene pyrolysed for 2 s at 500°C. The main product was butadiene and the second vinylcyclohexene (dimer). Column temperature: 120°C.

Fig. 4. Curve 1: yield of butadiene formed versus amount of polybutadiene pyrolysed. Curve 2: calibration graph for polybutadiene pyrolysed together with 5 μg of polystyrene. The standard deviation is marked where it is larger than the symbols used.

longer pyrolysis times. However, secondary reactions caused an undesirable deviation with larger amounts of sample, which did not occur at the lower temperatures.

Poly(methyl methacrylate)

When pyrolysing poly(methyl methacrylate) in microgram amounts both the total yield and the yield of the monomer (MMA) are virtually constant from 500 to 700°C [15]. Possibly, the catalytic effect of the metal foil could be lower at lower temperatures, so various amounts of poly(methyl methacrylate) were pyrolysed at 470°C for 2 s. In the pyrogram shown in Fig. 5 it can be seen that the main product is the monomer, which constitutes ca. 98% of the total yield detected. The area of the MMA peak was plotted logarithmically versus the amount of poly(methyl methacrylate) pyrolysed (curve 1 in Fig. 6). The calibration graph was linear between 5 and 20 µg, and 0.1 µg could be detected.

To increase the yields of MMA for the smallest samples, polystyrene was added to the sample solutions to give 5 µg of polystyrene in the samples to be pyrolysed. The improvement achieved can be seen in Fig. 6 (curve 2). The curvature of the calibration graph was decreased and the detection limit extended to 10 ng of poly(methyl methacrylate), where the standard deviation was 30% (see the marking on curve 2). The samples were also pyrolysed

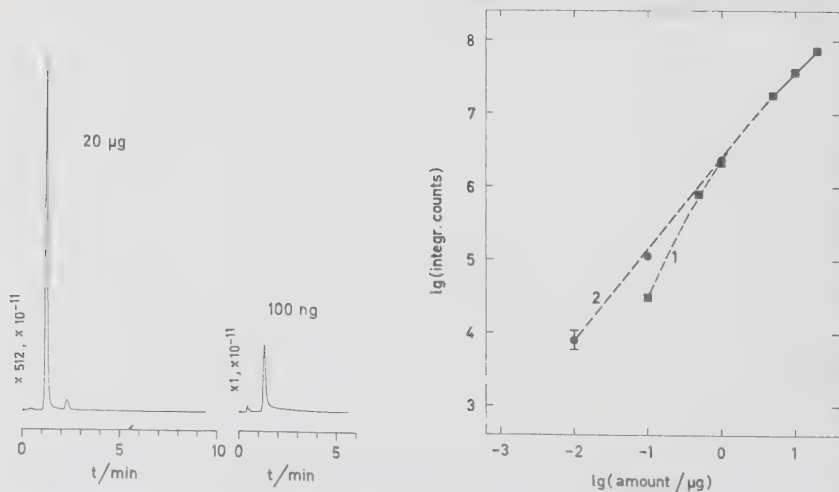


Fig. 5. Pyrograms of poly(methyl methacrylate) pyrolysed for 2 s at 470°C. The main product was methyl methacrylate.

Fig. 6. Curve 1: yield of methyl methacrylate formed versus amount of poly(methyl methacrylate) pyrolysed. Curve 2: calibration graph for poly(methyl methacrylate) pyrolysed together with 5 µg of polystyrene. The standard deviation is marked where it is larger than the symbols used.

at 675°C for 8 ms. The results were almost identical with those obtained at 470°C.

This polymer behaves differently from the other two. After the addition of polystyrene the deviation of the calibration graph was decreased, but the linear range was not extended noticeably.

Pyrolysis of μg — mg samples

The most suitable pyrolysis conditions for large sample sizes were different from those for smaller amounts. The optimal temperatures were chosen to be the highest possible, i.e., where the yield is not decreased, to allow as short a pyrolysis time as possible. The following experiments were performed using the foil with the cavity in it.

Polystyrene

For polystyrene, 2-s pyrolyses at 800°C were found to give high and reproducible monomer yields and total yields. After recording the pyrogram the pyrolysis procedure was repeated until no products were formed, at most four times.

From 5 to 1340 μg of polystyrene were pyrolysed under these conditions. The yield expressed as the integrated area of the styrene peak per microgram of sample was plotted versus the amount of polystyrene pyrolysed (Fig. 7a). The yield decreased by 35% between 5 and 400 μg , whereafter it remained relatively constant. Illustrated as an ordinary calibration graph (Fig. 7b), the result was a slight bending in the initial part and then a straight line.

To decrease the total time of the analysis, longer continuous pyrolysis times were tested, but this gave lower yields. Higher pyrolysis temperatures also diminished both the total yield and the monomer yield. At low temperatures the monomer yield is not maximal. The thicker the sample is, the lower will its temperature be, which explains the decrease in Fig. 7a.

Polybutadiene

It was found optimal to pyrolyse large amounts of polybutadiene at 1000°C for 1 s, repeatedly when necessary. Five times were enough for the largest samples. Samples of 5–1690 μg were run. The yield of butadiene per microgram of polybutadiene decreased with the amount of sample (Fig. 8a). This resulted in a calibration graph bent over the whole range of sample sizes (Fig. 8b), but the graph was still unambiguous. With a 2-s pyrolysis time, which would reduce the total time of the analysis, the yield of monomer was lower, but the result would still be usable for quantitative analysis.

Polybutadiene has also been shown to be sensitive to secondary effects from the hot platinum foil [14]. When the time of each pyrolysis remains constant, the larger the sample the lower will be the temperature. To investigate whether the decrease in the yield was due to a catalytic effect or caused only by the temperature, 100 μg of polybutadiene were mixed with ca. 1 mg of polystyrene. The yield of butadiene per microgram of polybutadiene pyrolysed was the same as for samples of the same total size of pure poly-

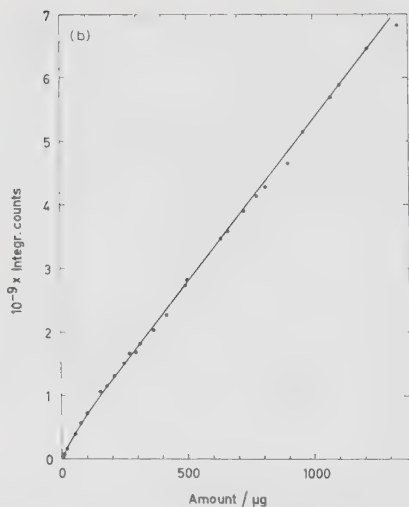
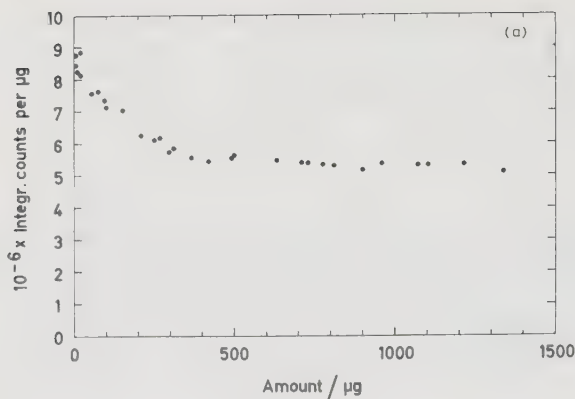


Fig 7. (a) Yield of styrene per microgram of polystyrene pyrolysed versus amount of polystyrene. (b) Yield of styrene versus sample size.

butadine. This result indicated that the effect was a primary reaction depending only on the temperature. Further, the detector could be excluded as a cause of this effect.

Poly(methyl methacrylate)

A maximal yield of the monomer (MMA) was obtained with a pyrolysis time of 1 s at 700°C, although the pyrolyses had to be repeated up to 20 times for the largest samples before all of the substance was degraded. The

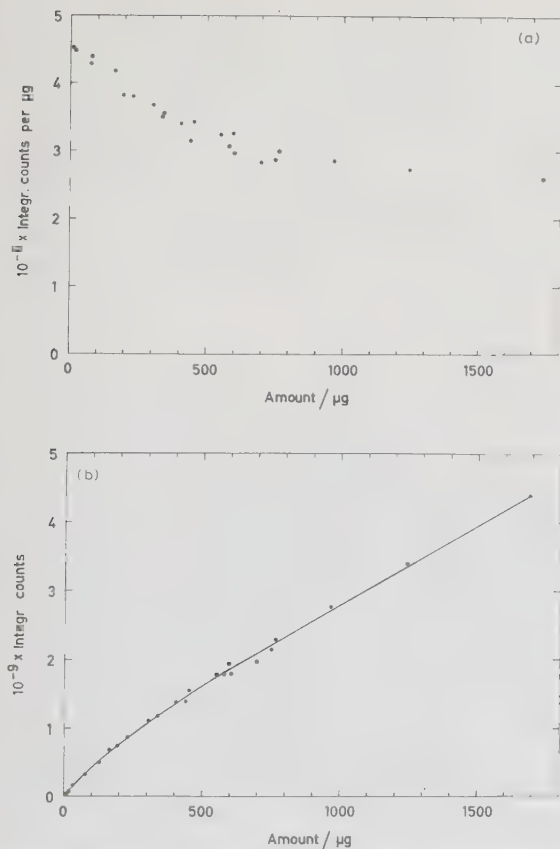


Fig 8. (a) Yield of butadiene per microgram of polybutadiene pyrolysed versus amount of polybutadiene. (b) Yield of butadiene versus sample size.

yield of MMA per microgram of PMMA pyrolysed was plotted versus the amount of polymer pyrolysed (Fig. 9a). The yield was fairly constant over the whole range of sample sizes investigated. The result was a straight-line calibration graph (Fig. 9b).

As mentioned above, the yield-temperature profile of MMA formed is constant over a wide temperature range up to ca. 800°C, where more fragments lighter than the monomer are formed and later where carbonization begins. Therefore, the low temperatures in the larger samples do not affect the yield. As the pyrolysis temperature was chosen where the yield is maximal for small samples, the calibration graph was linear over the whole range of sample sizes. If the pyrolysis time was increased to 2 s (at 700°C), some secondary reactions occurred, so that the yields of both the monomer and the total pyrolysis products decreased substantially.

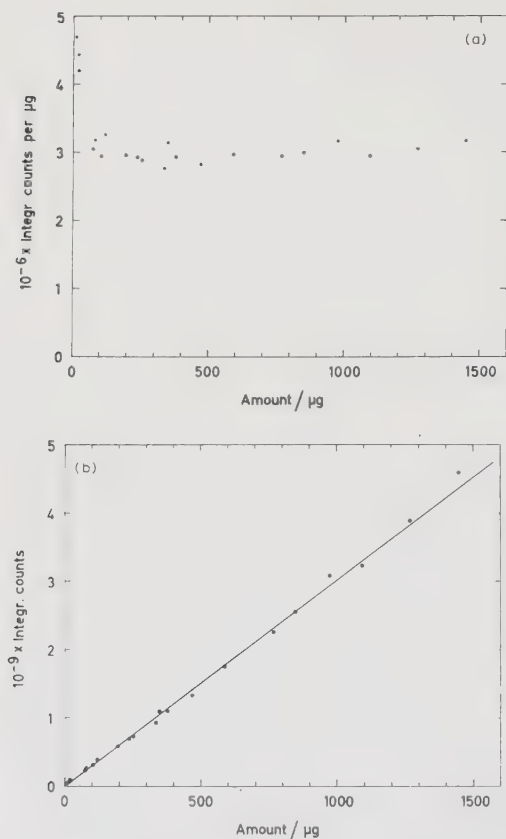


Fig. 9. (a) Yield of methyl methacrylate per microgram of poly(methyl methacrylate) versus amount of poly(methyl methacrylate). (b) Yield of methyl methacrylate versus sample size.

CONCLUSION

For each analytical problem the pyrolysis conditions have to be carefully chosen. The optimal conditions depend on the substance to be analysed and its amount.

With a suitable choice of pyrolysis time and temperature, nanogram amounts of sample can be analysed, although the yield of pyrolysis products is lower than expected owing to detector or catalytic effects. The result can be improved if another substance is added to the sample to be pyrolysed, provided that it is possible to differentiate the pyrolysis products of the latter from those of the former. This could be done either on the column or with a specific detector.

It is also obvious that up to milligram amounts could be pyrolysed to give unambiguous calibration graphs that can be used for quantitative analysis with a relatively small uncertainty. The greatest yields are obtained if pyrolysis pulses of relatively short duration are repeated. For practical applications where the maximal yield is unnecessary, the temperature could be higher or the pyrolysis time longer, both reducing the time of the analysis. The present results with high yields of pyrolysis products could be obtained provided that the temperature rise time is short, avoiding too much time spent at low temperatures, where volatilization of larger fragments could compete with the pyrolysis.

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A STUDY OF THE THERMAL DEGRADATION OF ORGANIC POLYMERS
WITH DIFFERENT METALS AS PYROLYSIS FILAMENT

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SUMMARY

Samples of polystyrene, cis-1.4-polybutadiene, poly(methyl methacrylate) and polyacrylonitrile were pyrolyzed on filaments made from iron, nickel and platinum. Iron generally gave the highest yields of pyrolysis products. Nickel gave high yields at low temperatures, but at higher temperatures the secondary degradation became important. Platinum generally gave the lowest yields.

Two sample sizes, 5 and 0.5 μg , were used to make it possible to separate the effects of catalysis from pure temperature effects.

INTRODUCTION

The foil in filament pyrolyzers is usually made from platinum. In Curie point pyrolyzers ferromagnetic materials, i.e. pure metals and alloys of e.g. iron, nickel and cobalt are utilized. As all these materials act as catalysts in different reactions, there is the possibility that they could catalyze the pyrolysis reactions as well. This effect has been discussed but in most cases no effects were seen. Dimbat et al [1] obtained the same pyrolysis pattern from polystyrene pyrolyzed on a platinum filament and a glass covered filament. Jones et al [2] found no indication of catalysis on the formation of the monomers and lighter fragments of poly(methyl methacrylate) and polystyrene pyrolyzed in microgram amounts

on filaments of nichrome, platinum and gold plated platinum. In the milligram scale of polymer the gold plated nichrome filament yielded simpler pyrograms. In a later work [3] Jones and Reynolds mixed the polymers with nichrome powder to obtain a large polymer to metal surface, but obtained the same pyrograms as with the pure polymers at the 5 μg level. Bell et al [4] varied the sample thickness from 40 to 300 nm of polyacrylonitrile and obtained constant yields of acrylonitrile and methacrylonitrile respectively, which would indicate lack of filament catalysis. However, in some cases effects have been observed, e.g. Prosser [5] reported variations of the peak sizes when 3 g of polyvinylidene fluoride was heated to 450°C together with 32 g and 40 g copper metal powders. Perry reported that the pyrolysis of polyethyleneglycols was markedly influenced by iron oxide [6]. Pozdnyakov et al [7] pyrolyzed poly(methyl methacrylate), polystyrene and poly(alpha-methylstyrene) on a tantalum ribbon varying the sample thickness from 0.1 to 20 nm, and determined the activation energies for the monomer formation. No catalytic effect was observed on polysytrene and poly(alphamethylstyrene). Poly(methyl methacrylate), however, showed lower activation energies for the thinnest samples, indicating a catalytic effect from the tantalum.

In earlier papers [8,9] we found that platinum probably had a catalytic effect on the pyrolysis of polystyrene, polybutadiene and poly(methyl methacrylate). The effects have therefore been studied more in detail for some common pyrolyzer

materials, iron nickel and platinum.

EXPERIMENTAL

Pyrolysis apparatus and working conditions

A detailed description of the pulse pyrolyzer has been given in an earlier paper [10]. The metal foil could easily be changed. Foils made of iron, nickel and platinum were used. The pyrolysis temperature, defined as the temperature at the middle of the foil, was determined with a photodiode, and for long pyrolysis times at low temperatures, from the resistance change of the foil [11]. The photodiode had been calibrated for temperature measurements on platinum. The calibration for iron and nickel was obtained by use of Stefan-Boltzmann's law which contains the emissivity of the actual foil. The total emissivity of nickel is 1.25 times that of platinum between 25°C and 1000°C [12]. This was used to evaluate the temperature of the nickel foil. The emissivity of iron as reported in the literature [12,13], varies greatly, depending on the surface condition. As the surface was less well defined in the present case, we also evaluated the temperature from the known rate of degradation of polybutadiene [14]. It seemed reasonable to use the factor 1.2 for the ratio of the emissivities between iron and platinum. This factor is also obtained from the spectral emissivities of iron and platinum at 0.65 μm [12]. Any error in the emissivity

estimation will move the temperature scale for that metal and will affect all the reported values to the same extent.

The pyrolyses were made with a constant heating rate. The pyrolyzer reached 1000°C after 8 ms. By interrupting the current after 7, 6 and 5 ms respectively, the end temperatures became 875 , 750 and 625°C respectively. For the experiments with long pyrolysis times the temperature rise time was 8 ms.

Sample preparations

The polymers were cis-1.4-polybutadiene, PB, (Cariflex 1220, Shell Chemicals, Berre, France), $\bar{M}_w=520\ 000$), polystyrene, PS, (a technical product, the Swedish Polystyrene Factory Ltd, Kävlinge, Sweden, $\bar{M}_w=260\ 000$), polymethyl methacrylate, PMMA, (Bead Polymer, Polyscience Inc., Warrington, PA U S A, Low Molecular Weight), and polyacrylonitrile, PAN (Polyscience Inc.). PS, PB and PMMA were dissolved in toluene. PAN was dissolved in N,N-dimethylformamide. $1\ \mu\text{l}$ solution of suitable concentration was applied to the foils. The solutions spread over an area of about 6mm^2 , which implies that the sample thickness varied when the concentration changed. The sample sizes were 5 and $0.5\ \mu\text{g}$, which correspond to a thickness of 1 and $0.1\ \mu\text{m}$.

Chromatographic conditions

Gas chromatograph: Varian 1860

Detector: FID

Hydrogen flow rate: 20.0 ml/min

Air flow rate: 240 ml/min

Carrier gas (nitrogen) flow rate: 20.0 ml/min

Pyrolysis chamber temperature: 180°C

Detector temperature: 275°C

Columns: Apiezon L, 2% on ULTRA-BOND 20 M, 100-120 mesh

1.5 m x 1/8 in. O.D., 1.9 mm I.D. steel column

temperature: 60-250°C, 15°C/min for PS, PB, PMMA, PAN

Chromosorb 102, 80-100 mesh, 1.0 x 1/8 in. O.D.,

1.9 mm I.D. steel column

temperature: 60-200°C, 15°C/min for PB, PAN

200°C isothermal for PMMA

Mass spectrometer: Finnigan 4021

Quantitative evaluation: When possible the integrator Varian CDS 101 was used. In case of severe baseline drift the peak height was measured.

With the Apiezon L column high-boiling products, dimers and trimers, were obtained, while the Chromosorb 102 was used to separate the volatile products.

RESULTS

The main pyrolysis products of polystyrene have been identified earlier for similar chromatographic conditions [15]. The pyrolysis products of polybutadiene were thoroughly identified by Braun and Čanji [16]. The pyrolysis products of PMMA marked in the figure were identified with mass spectrometry.

Mass spectra were also run on the separated products of pyrolyzed PAN. The results were consistent with those found in the literature [17,18,19].

Temperature dependence

The polymers, (5 and 0.5 μg of each), were pyrolyzed for 5, 6, 7 and 8 ms as described above. Figures 2-6 show the temperature dependence for the volatile products, the monomer, the dimers and the trimer and as well as for some other products formed from PS. The pyrolysis is not complete on any of the foils at the lowest temperature. Repeated pyrolysis increased the yields substantially for the platinum foil, and to a smaller degree for the others.

Figures 7-10 show the temperature dependences for the volatile pyrolysis products, the monomer, the dimer and some high boiling products of PB. PB has the property that at each temperature up to 1000°C there is a limiting yield [20].

In the described experiments no more products were found on repeated pyrolysis at each temperature, with the exception of a slight contribution at 625°C.

The temperature dependence of the pyrolysis products found of PMMA is illustrated in figures 11-12, which show the yields of the volatile products and the monomer. PMMA is the least thermostable of the polymers tested here [21]. The influence of the temperature on the yields of the pyrolyzates of PAN is shown in figures 13-16. The curves shown are for some volatile products, the monomer, the dimers and for the high-boiling products, probably trimers. There is an increasing yield of monomer with the temperature for all the three metals. Repeated pyrolyses did not increase the monomer yield. PAN is another example of a polymer giving limiting yields depending on the temperature [4]. As the high-boiling products were separated on an unpolar column, adsorption effects for the polar products were evident (fig. 1 f). Thus the values of the total yield could be too low. Despite this it should be possible to make comparisons between the three metals as the conditions were the same.

Influence of the pyrolysis time

To investigate whether the pyrolysis time was as important a factor as the temperature for the secondary reactions, the pyrolysis time was varied from 8 ms (=the temperature rise time) to 10008 ms.

5 μg PMMA was pyrolyzed on platinum and nickel at 620°C , where the yield was high but still the possibility of secondary reactions could exist. To increase the possible influence from the metal surface the experiments were repeated with the smallest detectable amounts that yielded reproducible results, i.e. 100 ng on platinum and 10 ng on nickel. The monomer yields, plotted in fig. 17, show no greater variation with the heating time for the larger samples.

The time dependence was also studied for PAN pyrolyzed on Ni and Pt at a low pyrolysis temperature (640°C). For this sample the yields were low. Similar observations as described above were made. No significant variation was noted.

DISCUSSION

The effect of the material of the pyrolyzer could consist in:

Physical influence. The heat capacity determines the rate of heating and cooling. The shape of the foil affects the probability for the products to touch the hot foil. In the present case the heating rates were made equal for the three metals by adjusting the amplitude of the first current pulse.

Chemical influence. The metal catalyzes the formation of primary as well as secondary pyrolysis products. Catalysis implies that the rate constants of the reactions are altered.

Different catalysts favour different reaction paths resulting in different yields of products formed on the three metals. Thus, the catalysis could affect the following reactions:

The primary degradation, yielding different amounts of primary pyrolysis products. The effect should be enhanced when using a thin sample.

The secondary degradation. The effect is seen as an increased yield of especially more low-boiling components, which are formed from degradation of primarily formed products.

Dehydrogenation, which implies increased yield of unsaturated products. Carbonization can also be regarded as a dehydrogenation reaction. With a flame ionization detector carbonization is seen only indirectly as a lowered total yield.

Hydrogenation. Hydrogenation should increase the yields of saturated compounds. The hydrogen source can be dehydrogenation reactions of the sample or the impurities in the carrier gas.

The present choice of the temperature-time profile of the foils make it possible to study both the primary and secondary reactions. There is a linear increase in temperature with time during a pyrolysis. Depending on the time of the current pulse various end temperatures are reached. The initial

part of a pyrolysis ending at a high temperature is therefore the same as the complete reaction during a pyrolysis ending at a low temperature. The additional time spent at high temperatures can either give additional primary reaction products or cause secondary reactions for products formed during the initial part of the run.

All the three metals are known to be catalysts, although with different activity, for hydrogenation and dehydrogenation reactions, due to their abilities to adsorb both hydrogen and olefins [22]. The rate of ethylene hydrogenation increases in order $\text{Fe} < \text{Ni} < \text{Pt}$.

Iron

High total yields were obtained with iron for all the samples studied, see fig. 2, 7, 11, 13, which implies that little degradation into nondetectable products occurred. This is especially the fact at high temperatures. The secondary decrease of the total amount was rather slow, indicating only moderate carbonization.

The monomer yields of the 0.5 μg sample were about 0.1 times that of the corresponding 5 μg samples. The smaller samples gave higher relative yield at low temperatures, see fig. 7. The reason is that the smaller sample reaches a higher temperature than the thicker.

Nickel

At low temperatures the highest yields were obtained with nickel, fig. 7, 11, 13. The yields of primarily formed products decreased rapidly at higher temperatures, fig. 2 c d, 5 a b, 7 c d, 9 a b, 11, 16, 16. Errors in the temperature determination or slow cooling due to the high heat capacity of nickel should not produce effects of this size. The most likely explanation is that the secondary carbonization reactions have high activation energies.

The direct surface effect of nickel is not very great as indicated by the similarity of curves of the two sample sizes. The only exception is the oxygen-containing MMA, for which there is a lowered relative yield for the 0.5 μ g sample also on Ni, fig. 11.

Platinum

With platinum the total yields were low, especially for the thin 0.5 μ g samples, fig. 2 b, 7 b, 11 b, 13 b.

The monomers give the largest contribution to the total yield for all the polymers studied here. Therefore low monomer yields imply low total yields. Also large fragments, dimers and trimers, fig. 5, 6, 15, 16 were formed in small amounts on platinum.

The secondary decrease of the total yields was small for platinum. This implies that if carbonization is the cause of the low yields, it is a primary reaction with low activation energy.

Comparison of the three metals

As to the primary monomer formation with the larger sample size the maximum yields do not diverge much between three pyrolyzer materials. The maximum yields for the 0.5 μg samples in most cases decrease in the order $\text{Ni} > \text{Fe} > \text{Pt}$.

Less volatile primary products, i.e. dimers and trimers, are formed in greatest extent on iron, fig. 5, 6, 9, 10, 15, 16. In the present examples platinum reduces the amount of trimers, fig. 6 and 16.

The secondary formation of lighter fragments is generally favoured by nickel, fig. 3 a, b, 8, 12 a, 14. Platinum and iron give somewhat lower yields. For nickel there is a secondary degradation (=carbonization) even of the lighter products, fig. 3 c d, 12 b c d, 14 d. The secondary degradation had a small time-dependence at the low temperatures, 620 and 640°C. At higher temperatures where the secondary degradation is more important, greater variations are observed [15].

The hydrogenated products, e.g. ethylbenzene S4, fig. 3, and C_9H_{10} S6, fig. 4, are formed in greatest amounts on platinum. This is in agreement with the function of platinum as a hydrogenation catalyst.

The dehydrogenation reaction, carbonization, implying low total yields, is obvious on platinum, especially with the thin samples. At high temperatures it is very noticeable also for nickel

Iron gives high yields, which implies that products from very thin samples could be detected. At low temperatures also nickel gives high yields. The great secondary carbonization on nickel could be detrimental for quantitative analyses. Platinum foils produce low yields, which restricts the range of sample sizes downwards.

However, platinum is the most convenient metal to handle. It can be simply and efficiently cleaned by heating in a bunsen flame. The resistance of a platinum foil remains unchanged after pyrolysis and cleaning which gives a stable temperature calibration. This advantages are lost when iron and nickel foils are used.

CONCLUSION

It has been shown that variations of the pyrolysis results do arise, depending on the materials of the pyrolyzer. The reason why this has escaped attention earlier could be that only relative yields of the main products are measured.

The pyrolysis temperature was seen to affect the results much more than the material of the pyrolyzer, provided the sample size was not too small ($> 1 \mu\text{g}$). Thus the material of the pyrolyzer is not a main factor for the comparison of results obtained with different pyrolyzers.

From the present results the possibility also arises to utilize pyrolysis gas chromatography as a pilot method for catalyzed processes.

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Fig.1a) Pyrogram of 5 μ g PMMA pyrolyzed for 7 ms (875°C). Column temperature: 200°C

Peak	MS identification
M1	C ₁
M2	C ₂
M3	C ₃
M4	C ₄ H ₈
M5	C ₅ H ₈ O ₂ monomer

b) Pyrogram of 5 μ g PS pyrolyzed for 6 ms, (750°C)

Peak	identity
S1	C ₁ -C ₄
S2	benzene
S3	toluene
S4	ethylbenzene
S5	styrene
S6	M _w =118
S7	M _w =116
S8	dimer
S9	- " -
S10	trimer

c) d) Pyrograms of 5 μ g PB pyrolyzed for 8 ms, (1000°C)

Peak	MS identification
B1	light fragments
B2	- " -
B3	- " -
B4	- " -
B5	butadiene
B6	vinylcyclohexene
B7	
B8	trimer
B9	- " -

e) f) Pyrograms of 5 μ g PAN pyrolyzed for 6 ms, (750°C)

Peak	MS identification
A0	light fragments
A1	acetonitrile
A2	acrylonitrile
A3	methacrylonitrile
A4	
A5	M _w = 119 dimers
A6	M _w = 106 - " -
A7	M _w = 106 - " -
A8	M _w = 171 trimer?
A9	- " -
A10	- " -
A11	- " -

Pyrolyses a - f performed with Pt

Column conditions: b, d, f, temperature programmed 70-250°C

15°C/min

c, e, temperature programmed 70-200°C,

15°C/min

Chromosorb 102

Apiezon L



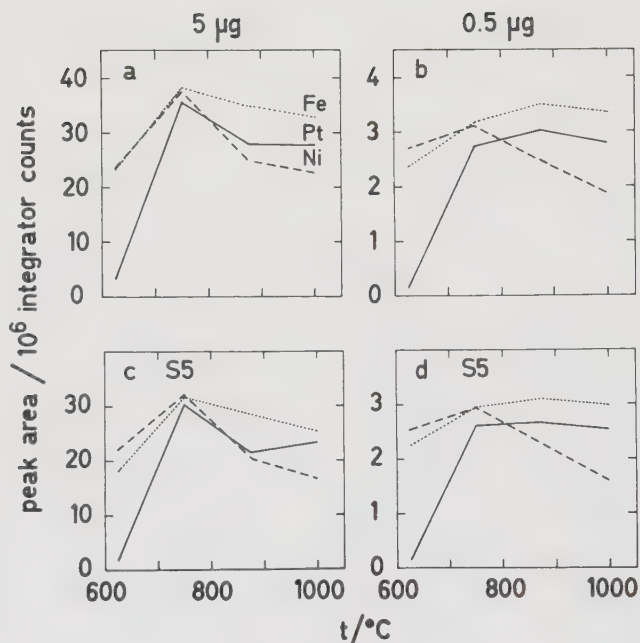


Fig. 2. The total yield of pyrolysis products from
 a) 5 μg and b) 0.5 μg PS and the monomer yield from
 c) 5 μg and d) 0.5 μg plotted versus the end temperature.
 Fe, --- Ni, — Pt

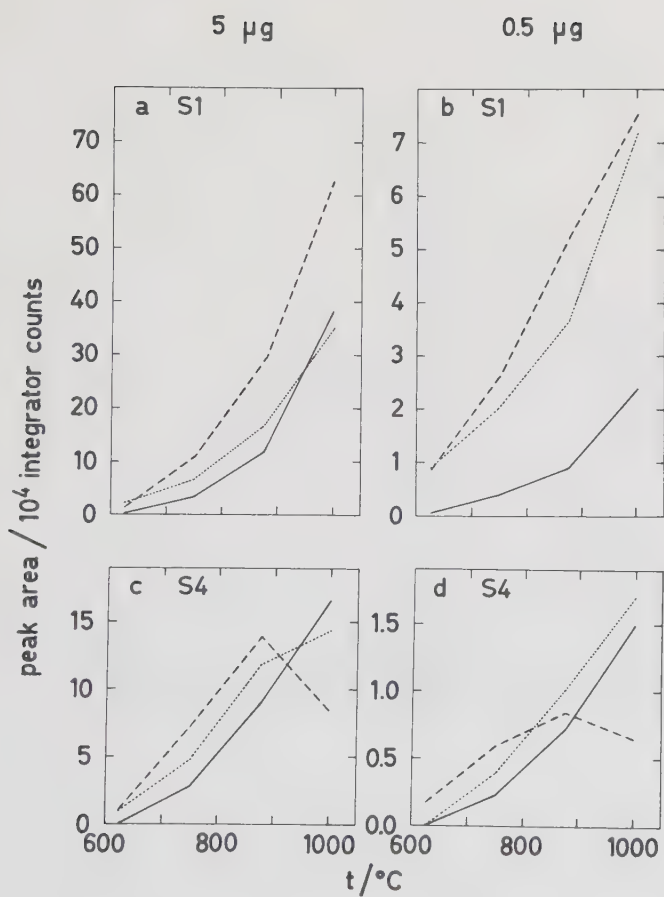


Fig. 3. The yields of C₁-C₄ a) b) and ethylbenzene c) d) from pyrolysis of PS plotted versus the end temperature.

... Fe, --- Ni, — Pt

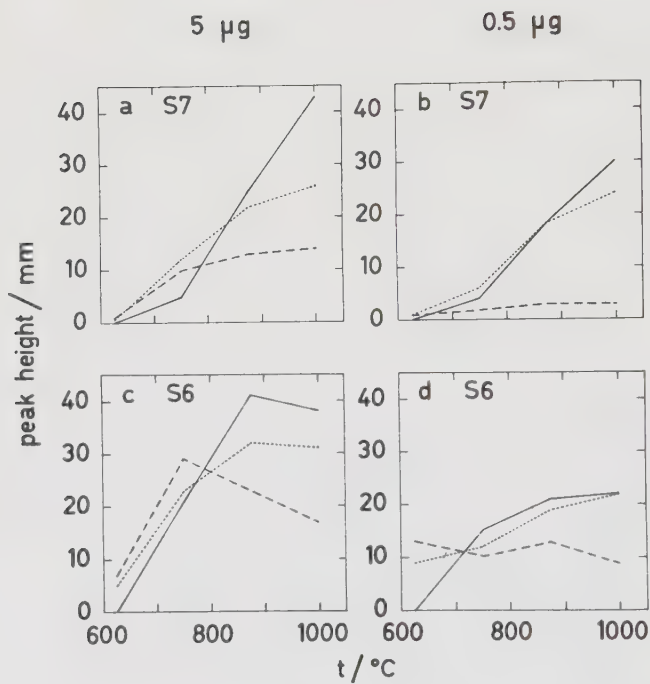


Fig. 4. The yields of the products with $M_w = 116$ a) b) and $M_w = 118$ c) d) from pyrolysis of PS plotted versus the end temperature.

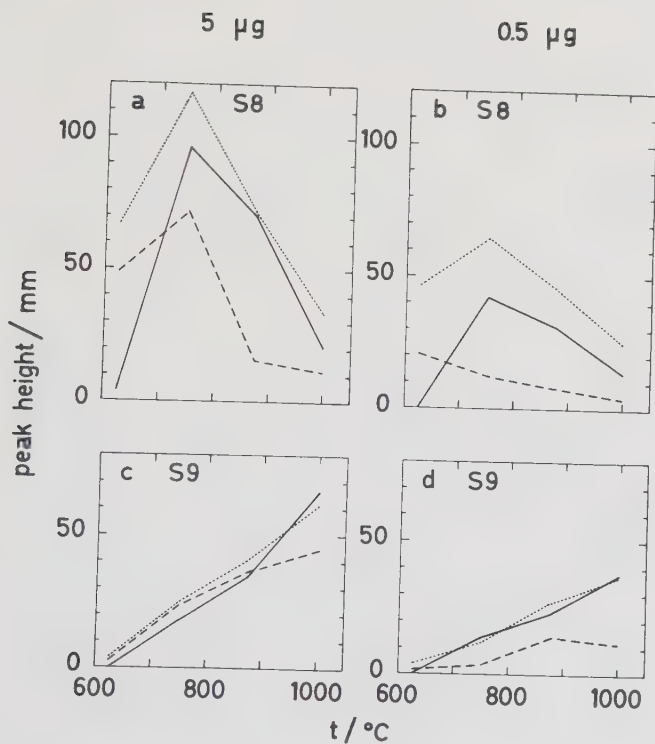


Fig. 5. The yields of the dimer 1 a) b) and the dimer 2 c) d) of PS plotted versus the end temperature.

... Fe, --- Ni, — Pt

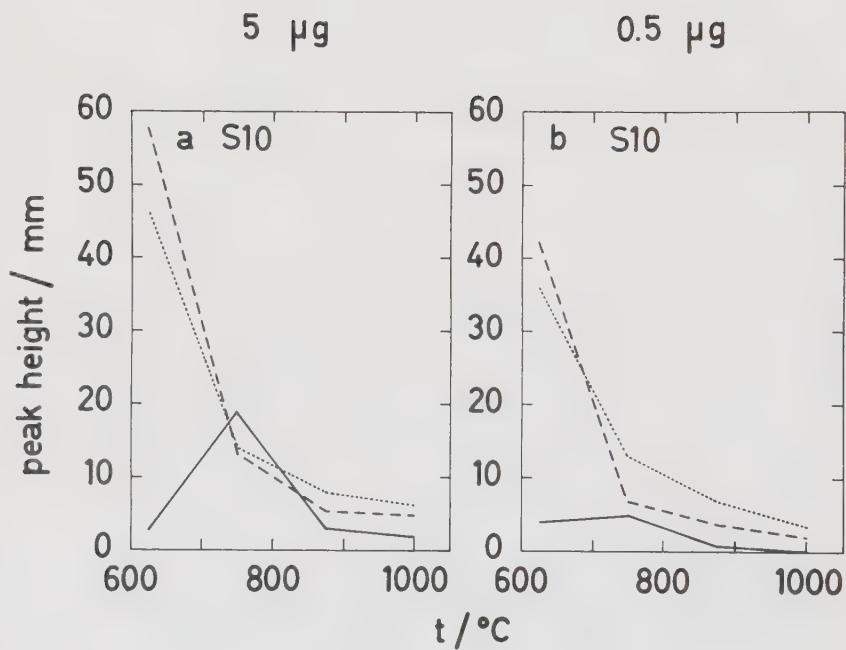


Fig. 6. The yields of the trimer of a) 5 μg and b) 0.5 μg PS plotted versus the end temperature.

... Fe, --- Ni, — Pt

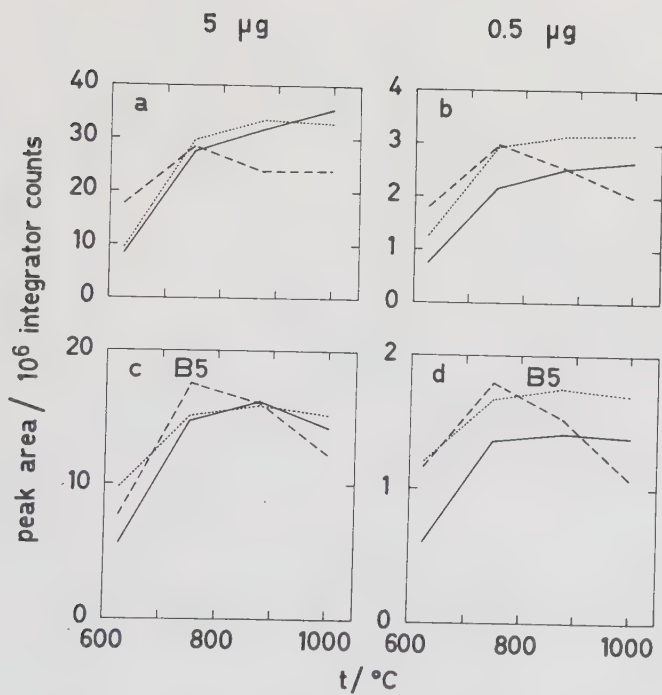


Fig. 7. The total yield of pyrolysis products from a) 5 µg and b) 0.5 µg PB and the monomer yields c) d) plotted versus the end temperature.

... Fe, --- Ni, — Pt

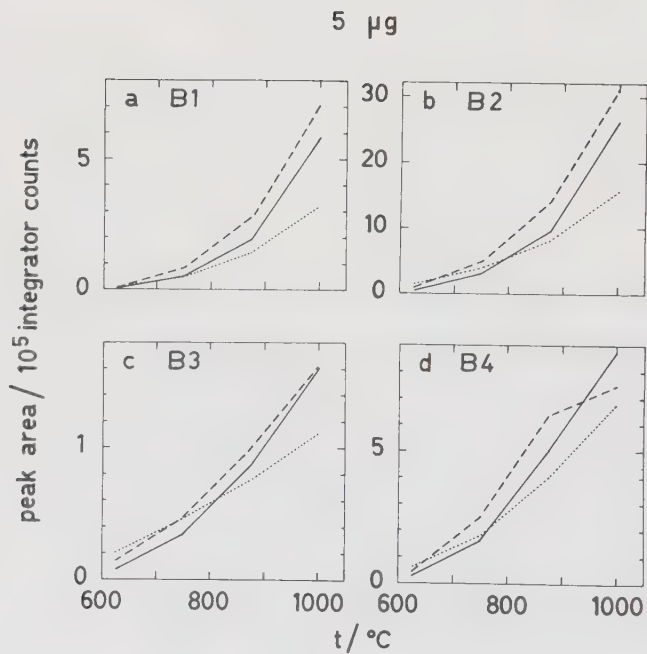


Fig. 8. The yields of light fragments from pyrolysis of 5 μg PB.

... Fe, --- Ni, — Pt

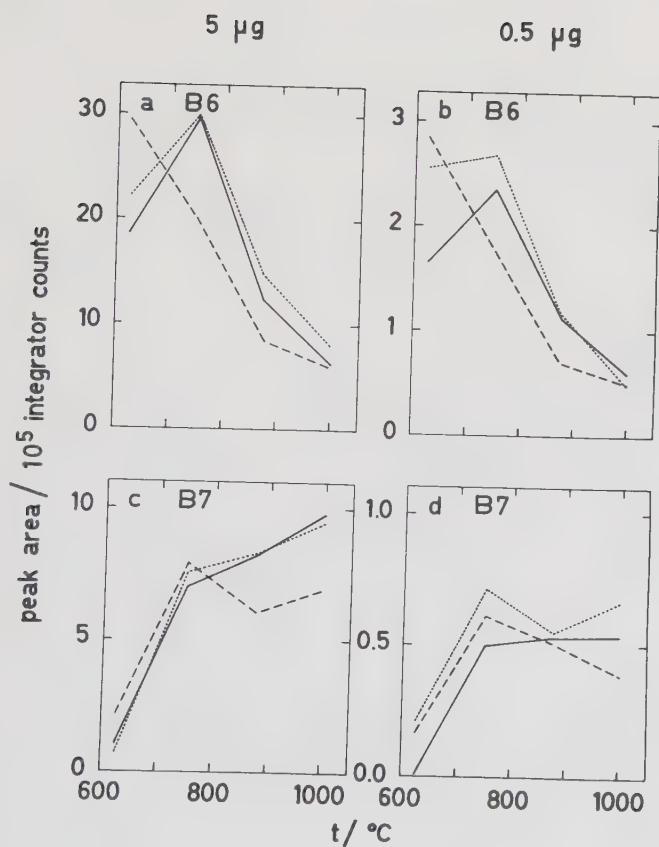


Fig. 9. The yields of the dimer a) b) and peak B7 c) d) from pyrolysis of PB plotted versus the end temperature.
 ... Fe, --- Ni, — Pt

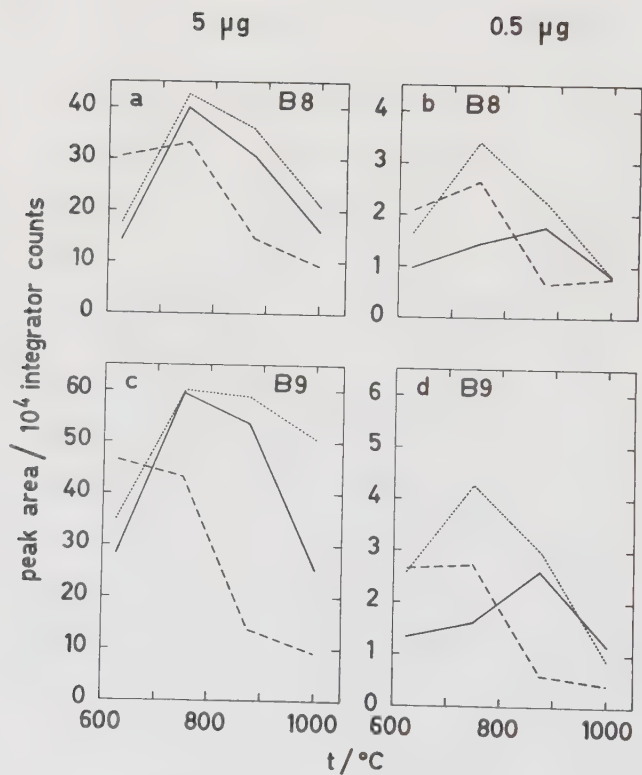


Fig. 10. The yields of the products marked B8 a) b) and B9 c) d) from pyrolysis of PB plotted versus the end temperature.

... Fe, --- Ni, — Pt

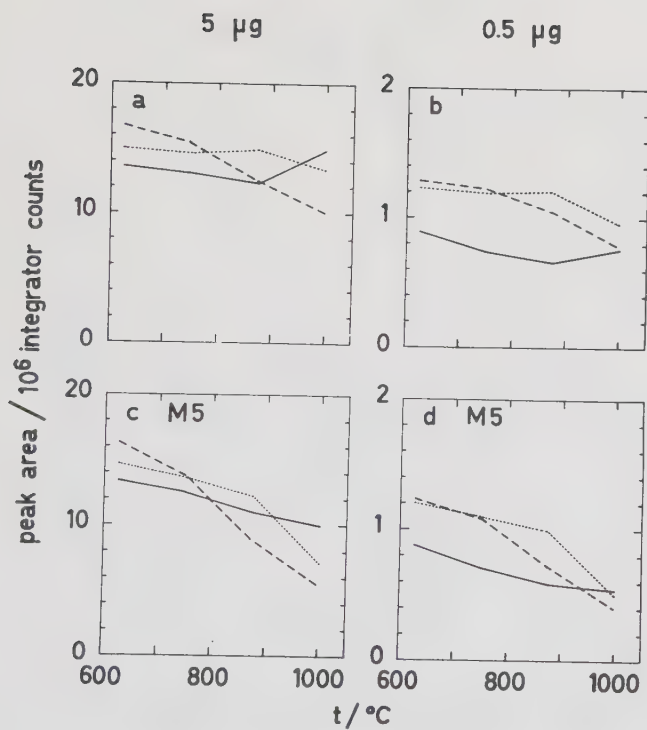


Fig. 11. The total yield of pyrolysis products from a) 5 µg and b) 0.5 µg PMMA and the monomer yields c) d) plotted versus the end temperature.

... Fe, --- Ni, — Pt

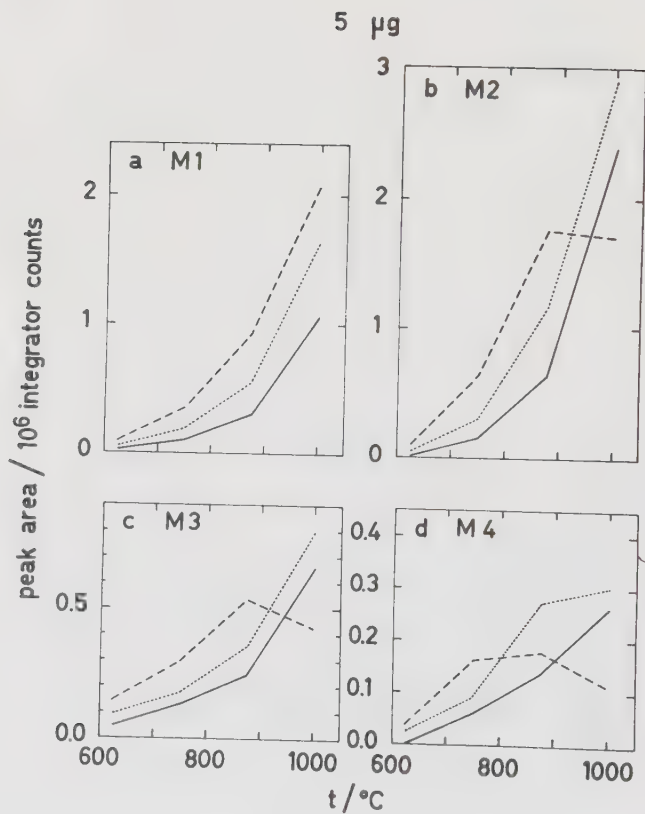


Fig. 12. The yields of volatile products formed from pyrolysis of 5 μg PMMA plotted versus the end temperature.

... Fe, --- Ni, — Pt

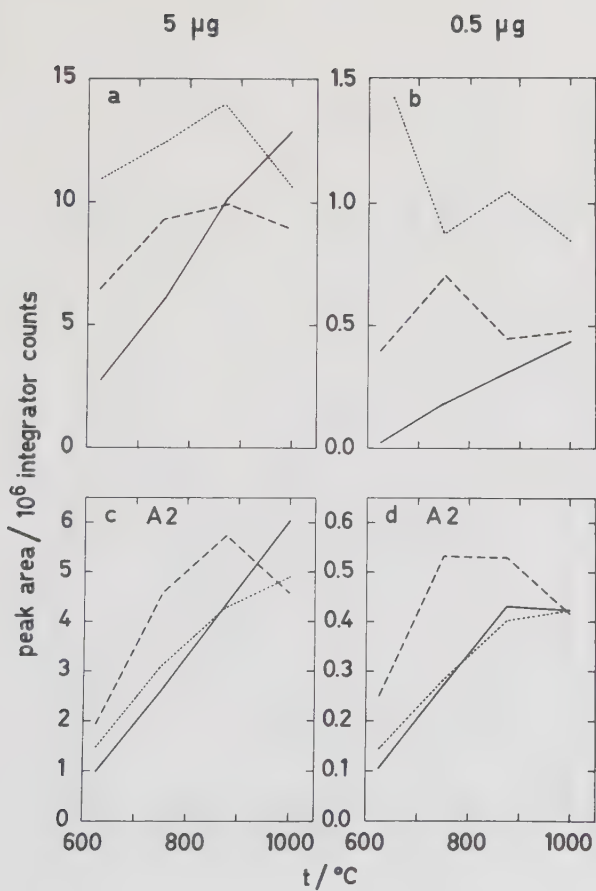


Fig. 13. The total yield of pyrolysis products from a) 5 µg and b) 0.5 µg PAN and the monomer yields c) d) plotted versus the end temperature.

... Fe, --- Ni, — Pt

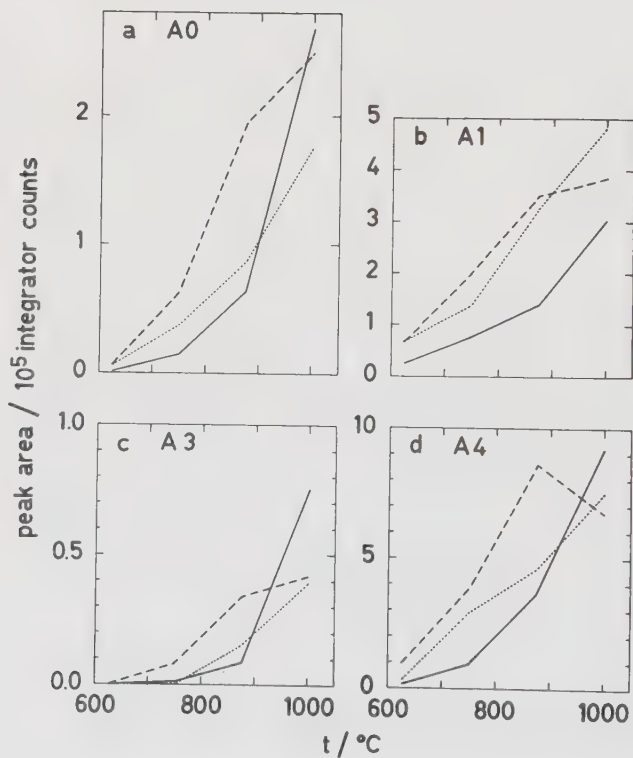
5 μg 

Fig. 14. The yields of light hydrocarbons a) acetonitrile b) propionitrile c) and methacrylonitrile d) from pyrolysis of 5 μg PAN plotted versus the end temperature.

... Fe, --- Ni, — Pt

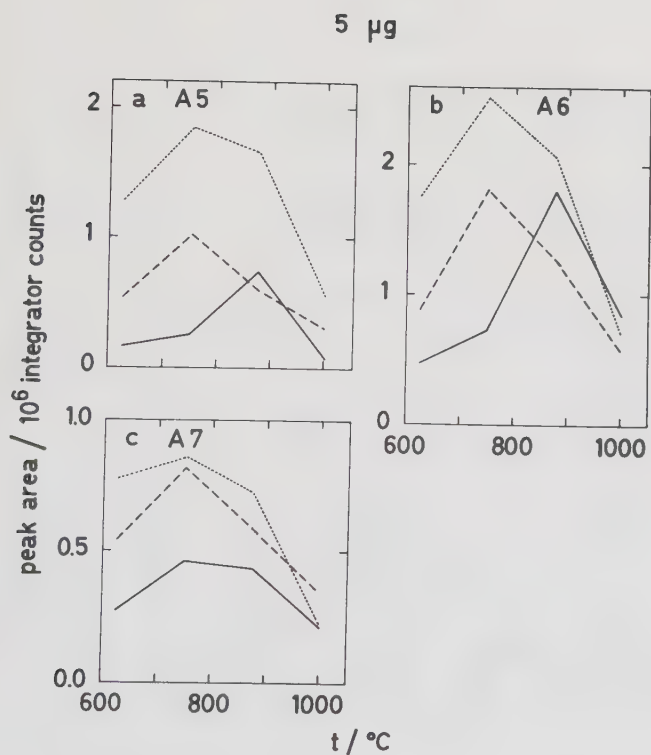


Fig. 15. The yields of the dimers from 5 μg PAN pyrolyzed plotted versus the end temperature.

... Fe, --- Ni, — Pt

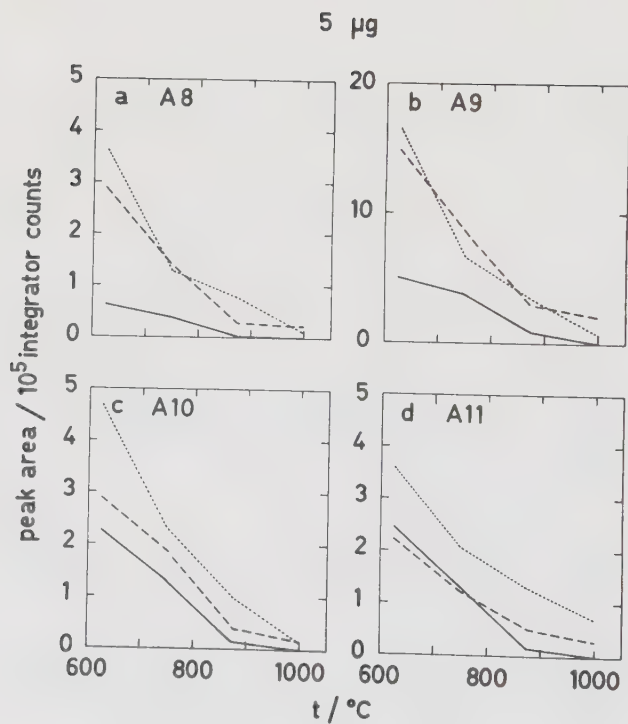


Fig. 16. The yields of the trimers from 5 μg PAN pyrolyzed plotted versus the end temperature.

... Fe, --- Ni, — Pt

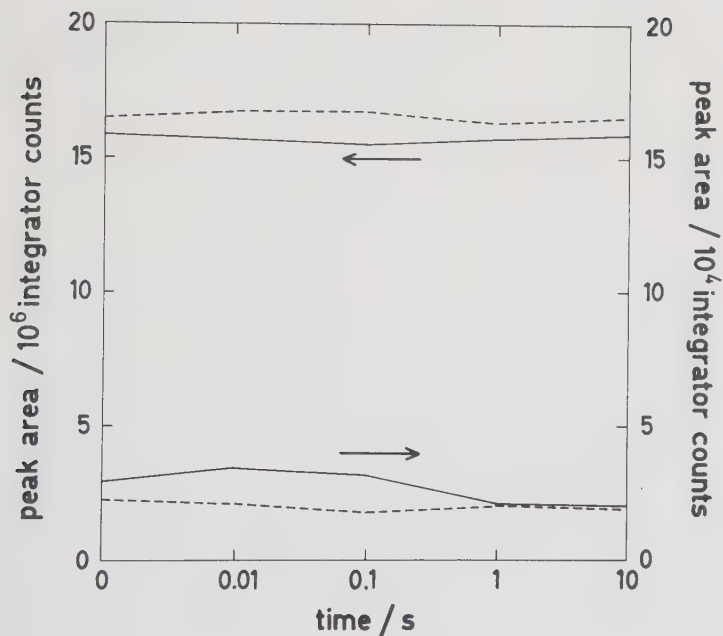


Fig. 17. The yields of MMA plotted versus the pyrolysis time for 5 μg PMMA pyrolyzed on platinum and nickel, upper curves, 0.1 μg pyrolyzed on platinum and 0.01 μg pyrolyzed on nickel, lower curves, at 620°C

--- Ni, — Pt

A STUDY OF SULFUR LINKAGES IN NATURAL RUBBER
VULCANIZATES BY PYROLYSIS GAS CHROMATOGRAPHY WITH
FLAME PHOTOMETRIC DETECTION

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SUMMARY

Natural rubber vulcanizates of two formulations, with CBS/sulfur and TMTD respectively, were analyzed by pyrolysis gas chromatography. A sulfur selective flame photometric detector was utilized. The main pyrolysis products were identified as CS_2 and some thiophenes. The yields of the pyrolysis products from the two types of rubber were very different. The yields also varied with the curing time of the rubbers.

INTRODUCTION

The thermal and mechanical properties of vulcanized rubber are strongly affected by the different types of crosslinks [1,2,3]. Direct methods for estimation of the structural properties of vulcanizates include measurements of physical properties [4] as swelling [5], creeping [6] and stress-strain [7,8]. Chemical "probes" are used in combination with stress-strain measurements [4,9,10] for the relative determination of the different types of crosslinks. Despite the existing methods, there is still a demand for improved procedures to determine the types and distribution of sulfidic bridges [4,9].

The pyrolysis technique is an established method for polymer analysis. A survey of the technique applied to analysis of insoluble samples, mainly vulcanized rubber has been made [11]. It has been shown that pyrolysis gas chromatography, PyGC, can be used with good reproducibility for the analysis of large [11,12] samples.

It was shown [11] that the sulfur content affected the yield of butadiene when vulcanized styrene-butadiene rubber was pyrolyzed. Häusler and Hube [13] found a correlation between the degree of swelling and the peak ratio toluene/4-vinylcyclohexene from PyGC measurements of vulcanized polybutadiene.

Recently Czybulka et al [14] studied vulcanizates by pyrolysis field ionization mass spectrometry with special attention to the components present in low concentration, viz. co-monomers, accelerators, metal oxides and antioxidants.

In the PyGC studies mentioned [11,13] the flame ionization detector was used. The sulfur containing pyrolysis products should be of special interest for the study of sulfur linkages. Sulfur containing products can be selectively detected with a flame photometric detector [15].

A flame photometric detector has earlier been used together with PyGC for quantitative determination of aliphatic sulfur-containing additives [16]. The additives were extracted from the polymer prior to pyrolysis.

The possibilities of direct qualitative and quantitative determinations of different sulfur-linkages of vulcanized rubber by pyrolysis gas chromatography was studied.

EXPERIMENTAL

Apparatys and operating conditions

The pyrolyzer consists of a thin (0.012 mm) platinum foil, 15 mm long and 2.6 mm wide. The edges of the foil were bent upward at the middle, in order to prevent the sample from falling off the foil. The foil was heated by two current pulses.

The first, 8 ms long, increased the temperature of the pyrolyzer to the desired pyrolysis temperatures. The second, the length of which could be varied, compensated for heat losses so that the temperature of the pyrolyzer was constant. The pyrolyzer was connected directly to the column of the gas chromatograph.

Pyrolyzer: Foil pulse [17]

Pyrolysis chamber temperature: 70, 115, 175°C

Pyrolysis temperature: 600, 800, 1000 and 1200°C

Pyrolysis time: 0.2 and 0.5 s

Gas Chromatograph: Varian 1860

Column: 3.5 m x 1/8 in., 1.9 mm I.D., stainless steel

Column packing: 10% Carbowax 20 M on Chromosorb W, AW,
80/100 mesh

Column temperature: Programmed 50-250°C, 20°C/min

Flow rates: N₂-20.0 ml/min, H₂-80 ml/min, Air-80 ml/min

Detector: Flame photometric - Micro Tek Instrument Corporation,
Austin, Texas

Detector temperature: 125°C

Integrator: CDS 101

Mass spectrometer: Finnigan 4021

The integrals of the registered peaks, measured by the integrator, are given in integrator counts, i.e.

Samples and Preparation

The formulations of the samples investigated are listed in Table 1. The samples named RA and RB were used as references as they had been analyzed for the crosslinks by RAPRA [18], Table 2. These samples had been vulcanized for 33, 50 and 66 min at 140°C. The RA and RB vulcanizates were treated with propane-2-thiol to cleave the polysulfidic crosslinks, and n-hexane-thiol to break the poly- and disulfidic crosslinks. The samples named SA and SB had been vulcanized at 140°C for 10, 30, 50 and 70 min.

The samples were Soxhlet extracted for 24 h with an azeotropic mixture of acetone, chloroform and methanol (3.52:2.91:2.74 by volume) to remove any residues of sulfurous compounds not combined in the polymer network. The samples were cut in small, thin pieces and weighed on a Sartorius microbalance. The samples weighed 35-45 µg.

The total sulfur content of the different samples was determined by elemental analysis [19].

For the identification of the pyrolysis products acetone-solutions of carbondisulfide, thiophene, 2-methylthiophene, 3-methylthiophene, methan-thiol and 2-propene-1-thiol respectively ($1:10^3$ by volume) were used. The injected volume was 1 µl. These solutions were also used to determine the detector response factors.

RESULTS

Test of chromatographic and detection conditions

Column packings of different polarity were tested. Carbowax 20 M on an unsilanized support was found to give a good separation and symmetric peaks of the sulfurous compounds, without any troublesome loss of high-boiling components. The sensitivity of the detector increased with decreasing flow rates of hydrogen and air. At too low air flow rates (≤ 60 ml/min) the flame became unstable. Equal flow rates of hydrogen and air of 80 ml/min were found to give a stable signal and high response factors for sulfurous compounds.

The relation between the detector response and the concentration of sulfurous compounds was determined. Eckhardt et al [15] showed that the response of the FPD was much dependent of the gas flows. Different concentrations of carbondisulfide solutions were injected. The logarithm of the registered peak area was plotted versus the logarithm of the amount of carbondisulfide injected. A straight line with the slope 2.0 was obtained. Consequently, the square root of the peak areas should be a linear function of the amount of sulfurous substances. The sulfur to carbon selectivity was estimated to be $4 \cdot 10^5$ from the detector response for carbondisulfide and acetone.

Identification of pyrolysis products

Fig. 1 shows examples of pyrograms obtained from the two vulcanizing systems. Many minor peaks, not seen at the present recorder attenuation, were registered by the integrator. The same pyrolysis products were obtained for all the vulcanized samples. The identification was made from comparison with retention data for injected sulfurous compound solutions. Mass spectrometry did not provide reliable identification due to the large background signals from the hydrocarbons.

Table 3 shows the molar response factors for the liquid products identified.

H_2S , CH_3SH and $\text{CH}_2 = \text{CH}-\text{CH}_2\text{SH}$ have earlier been suggested as possible pyrolysis fragments [14]. The retention times for these products coincide with the retention time for some products formed in small yields. Other thiophenes, thiols, sulfides and disulfides were tested. None of them gave retention data corresponding to peak no. 6, but to some of the small peaks between peaks nos. 5 and 6.

Natural rubber pyrolyzed together with elemental sulfur gave much the same pyrolysis products as the RA-samples. Natural rubber and carbon black together gave negligible peaks.

Pyrolysis chamber temperature

Samples of the RA- and RB-vulcanizates were pyrolyzed at chamber temperatures of 70, 115 and 175°C. The pyrograms

obtained at 70 and 115°C were very similar. The yields of high-boiling products did not increase at 175°C. Condensation of possible high-boiling products was therefore negligible. New reactions could not be ruled out as the temperature, 175°C, is much higher than the vulcanization temperature, 140°C. A chamber temperature of 115°C was therefore chosen.

Sulfur analyses

Table 4 shows the sulfur contents as determined by elemental analysis on the vulcanized rubber material. The table also gives the amount of sulfur expected from the formulations. To some extent the variation in the results can be explained by experimental errors, as only single determinations were made but the precision of the method is better than 2%. It is noteworthy, however, that larger amounts of sulfur were found than those calculated. The reason was that the carbon black and the natural rubber contained substantial amounts of sulfur. It is remarkable that the total amount of sulfur seems to increase with time of vulcanization both in the series made in our laboratory, Table 4, as well as in the series made by RAPRA, Table 2. The reason was not investigated.

Solvent extraction decreased the sulfur from samples of the RB and SB series substantially when the decrease for the RA series was small. When TMTD is used as a sulfur donor only a fraction of the sulfur content of it is combined in the network [9].

Treatment with the mercaptane to break the polysulfidic links results immediately in an additional adsorption of large amounts of sulfur. The following solvent extraction is supposed to remove all adsorbed sulfur but this seems to be questionable for the RA66 sample. The same can be said about the treatment with hexane-thiol.

Sulfur compounds produced during pyrolysis

All the analytical results were obtained with samples which had been extracted to remove soluble compounds e.g. residues from the TMTD and CBS.

The samples RA50 and RB50 were pyrolyzed at different pyrolysis temperatures. The time was chosen long enough to yield complete and reproducible pyrolysis for the sulfurous compounds, viz. 0.5 s at 600°C and 0.2 s at the higher temperatures. The yields of the main products are plotted versus the pyrolysis temperature in fig. 2.

The standard deviations for the different product yields are shown in Table 4. The variation of the yields from samples extracted on different occasions was not significantly greater than those from samples from the same extraction. No significant change of the yields was observed when the foil was changed.

The very reactive pyrolysis fragments of the present system could be the reason for the relatively high standard deviation.

Fig. 3 shows that the peak pattern is completely different for samples of the SA and SB series. RA and RB are essentially the same rubbers as SA and SB and Table 2 shows that the polysulfide content of the RA is dominating, whereas the RB series is dominated by the monosulfides according to the rather crude method used to obtain these percentages. The carbon disulfide dominates completely in the RB series of samples, Fig. 3, at all temperatures, Fig. 2. For the RA series on the other hand a great carbon disulfide formation sets in above 800°C . The methyl-thiophenes dominate at temperatures below 800°C . The amount of methyl-thiophenes increases with the vulcanization time.

A more detailed information is provided by the data in Table 6. The most striking feature is that the amount of carbondisulfide decreases drastically when samples of the RB series are treated with the bridge-breaking reagents. Another change for the RB series is noted in the amount of thiophenes which is increased by the disulfide breaking reagent.

The amount of carbondisulfide varies in a complicated manner for the RA series.

If the total amount of sulfurous pyrolysis products are summed together for measurements made at 1200°C it was possible to account for 98% of the sulfur found by elemental analysis.

The comparison was made on the RA50 sample with the response factors reported in Table 3 and with $7.5 \cdot 10^{-11}$ for other compounds. At temperatures less than 1200°C for the RA sample about 50% of the sulfur appeared as volatile compounds. For all temperatures of the RB series about 65% of the sulfur was detected.

DISCUSSION

Sulfur is bound into vulcanized rubber both as sulfidic bridges and as cyclic sulfides. If the Moore efficiency coefficient, ϵ , is taken - as is often done - as a measure of the proportion of cyclic sulfides, the amount should be only half as much in the RB series.

It is very likely that the methyl-thiophenes are formed from cyclic sulfides. It can be seen from Fig. 2 that they are easily formed at $600-800^{\circ}\text{C}$ in the RA sample. Much less is formed from the RB samples. The amount of methyl-thiophenes decreases at the very high temperature, possibly they are converted to thiophene itself. Cyclic sulfides are not necessarily the only source of thiophenes or methyl-thiophenes which is shown by the appearance of these compounds from an unvulcanized sample of natural rubber and sulfur. The disulfide breaking reagent also increased the amount of methyl-thiophenes for the RB series, see Table 6.

Another specific feature of the result is the varying production of carbondisulfide. Fig. 2 demonstrates clearly that again several reactions seem to be involved. With the results from only this early study available any explanations become necessarily very tentative. The RA sample, see Fig. 2, gives only very little carbondisulfide at 600°C in comparison with the RB samples. The production of carbondisulfide at 600°C could reflect the amount of disulfide bridges of the samples, although it should not be taken to mean that there will be a linear relation. The breakage of disulfide bridges, see Table 6, reduces the amount of carbondisulfide for the RB sample. The results for the RA samples in the Table are not directly comparable as the pyrolyses were made at 1000°C where other types of reactions seem to dominate.

Fig. 2 shows that the production of carbon disulfide from the RA samples increases rapidly until 1200°C where all the sulfur could be accounted for as volatile pyrolysis products. The number of polysulfide links is very high in the RA samples. It can also be assumed that each link contains several sulfur atoms so that most of the sulfur will be present as polysulfide. It is therefore tempting to correlate the onset of carbondisulfide production with the start of a reaction in which sulfide from the polysulfide chains takes part. Breakage of the polysulfide bridges in the RB sample seems at first to be accompanied by a corresponding decrease in the amount of

carbon disulfide. However, when the sulfur analyses in Table 5 are taken into account it is seen that the total amount of sulfur decreases in the same proportion, i.e. sulfur is removed in the extraction step. The same removal in the extraction step does not seem to occur with the RA samples although these are thought to contain much more sulfur in polysulfide chains. Thus, the propane-thiol reagent seems to attack also other links than the polysulfidic.

From a methodological point of view it can be seen already from this preliminary study that pyrolysis with a sulfur-selective detector can produce differences which can differentiate between various types of vulcanization, see Fig. 3. The progress of the vulcanization seems to be reflected in the results. So far, however, the properties have to be related to the differences in the pyrograms in a purely empirical way.

If the results are analyzed it can be seen that the diagnostic power of the method should have increased if a temperature of about 600°C also had been selected. If still lower temperatures are selected there will be a loss of information. If a sample was pyrolyzed for some time, 0.5 s, at 400°C, only very small amounts of sulfur containing compounds were obtained. If the residue was raised to 1000°C still no sulfur compounds could be seen. The sulfur had been lost, possibly as elementary sulfur which had condensed on the walls or in the column.

There are very few methods which can provide chemical information about insoluble synthetic polymers. The method described here provides a new information besides this available from other methods. A much more detailed study, including measurements on well-defined model compounds, is necessary before any definite conclusions about the reactions can be drawn. Considering the lack of chemical knowledge concerning vulcanized rubber such a study should be worth while.

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TABLE 1

Formulations of rubber materials. Weight parts per 100 parts of NR.

Vulcanization system	RA SA	RB SB
Natural Rubber, NR	100	100
Carbon Black, SRF	50	50
ZnO	5	5
Stearic Acid	1	1
CBS	0.6	-
Sulphur	2.85	-
TMTD	-	4

TABLE 2

Network analysis made by RAPRA. $S_{\text{total}}\%$: total sulfur content % (w/w). $S_{\text{sulfide}}\%$: inorganic sulfur % (w/w).

S_c %: sulfur combined in the network. ϵ : The Moore efficiency parameter defined by $S_c/\text{crosslink density}$.

Vulcanization system	RA			RB		
Time min ⁻¹	33	50	66	33	50	66
% polysulfide crosslinks	75	76	51	17	9	5
% disulfide crosslinks	25	24	49	29	31	22
% monosulfide crosslinks	-	-	-	54	60	73
S total% (w/w) (extracted)	1.96	2.12	2.22	0.82	0.74	0.80
S sulfide %	0.20	0.24	0.28	0.02	0.02	0.05
S_c %	1.76	1.88	1.94	0.80	0.72	0.75
ϵ	9.4	9.2	11.6	5.7	4.5	5.1

TABLE 3

Flame photometric detector response factors for
sulfurous compounds.

Substance	(Integrator counts) ^{$\frac{1}{2}$} per mole S
CS ₂	3.2 · 10 ¹¹
thiophene	6.3 · 10 ¹¹
2-methyl-thiophene	8.3 · 10 ¹¹
3-methyl-thiophene	8.5 · 10 ¹¹

TABLE 4

Sulfur content $\%$ (w/w). S_{calc} : calculated from the sulfurous compounds of the formulations
 S_{exp} : found by elemental sulfur analysis.

Vulcanization system	RA33	RA50	RA66	SA50	RB33	RE50	RB66	SB10	SB50	SB70	SRF	NR+SRF 2:1 w/w
Untreated samples												
S_{calc}	1.88	1.88	1.88	1.88	1.33	1.33	1.33	1.33	1.33	1.33	0	0
S_{exp}	1.97	2.20	2.32		1.57	1.71	1.61				0.46	0.34
Extracted samples												
S_{exp}	1.87	2.08	2.21	1.85	0.94	0.88	1.04	0.42	0.49	0.47		
After polysulfide cleavage												
S_{exp}			2.28				0.76					
After disulfide cleavage												
			1.85				0.85					

TABLE 5

The reproducibility obtained for the different pyrolysis products of the vulcanizate RA 33 during 3 weeks, $n = 13$. Pyrolysis at 1000°C for 0.2 s.

Peak no	1	2	3	4	5	6
$\bar{x}/\sqrt{i.c.} \times \mu\text{g}^{-1}$	2.96	25.4	29.0	11.2	21.2	9.20
S/%	10.7	13.0	8,8	4.4	4.3	11.5

The obtained yields of the products marked in Fig. 1 for the RA and RB vulcanizates pyrolyzed at 1000°C for 0.2 s. Samples marked "extracted" had just been extracted with the azeotropic solvent mixture, "polysulfide" were treated to break polysulfidic links before extraction, "disulfide" were treated to break both poly- and disulfidic links before extraction.

Peak no	Pyrolysis product	Sample preparation	RA33	$\sqrt{I.C.} \times \mu g^{-1}$		RA66	RB33	RB50	RB66
1	COS	extracted polysulfide disulfide	3.0 2.8 2.0	3.5 3.4 2.3		4.8 2.7 2.7	2.8 2.5 1.7	2.8 2.5 1.8	2.8 2.4 2.1
2	CS ₂	extracted polysulfide disulfide	25 33 22	28 37 27		31 35 44	45 34 25	43 35 25	43 35 26
3	thiophene	extracted polysulfide disulfide	29 25 20	30 26 30		28 27 32	6.1 8.8 11	8.1 7.4 14	7.6 8.0 13
4	2-methyl-thiophene	extracted polysulfide disulfide	11 9.8 6.6	13 12 11		13 9.7 12	2.1 2.5 3.1	2.8 2.2 3.7	2.5 2.4 3.6
5	3-methyl-thiophene	extracted polysulfide disulfide	21 18 12	22 21 20		22 17 21	5.7 6.8 8.5	8.0 6.8 9.5	6.9 6.9 10
6	?	extracted polysulfide disulfide	9.1 8.3 6.2	9.6 8.6 8.8		9.0 8.8 9.7	2.4 3.2 3.3	3.1 2.8 3.9	2.9 3.0 3.6

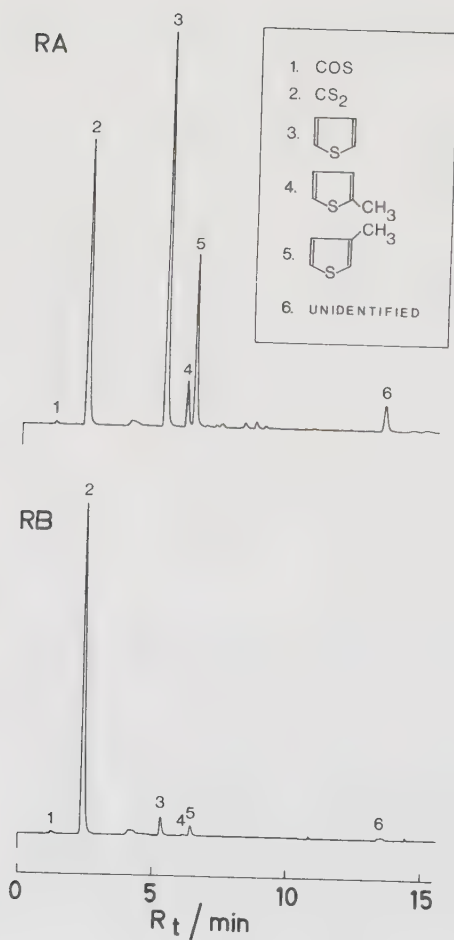


Fig. 1 Pyrograms of, 37 μ g of RA33 and, 33 μ g of RB33
pyrolyzed at 1000°C for 0.2 s.

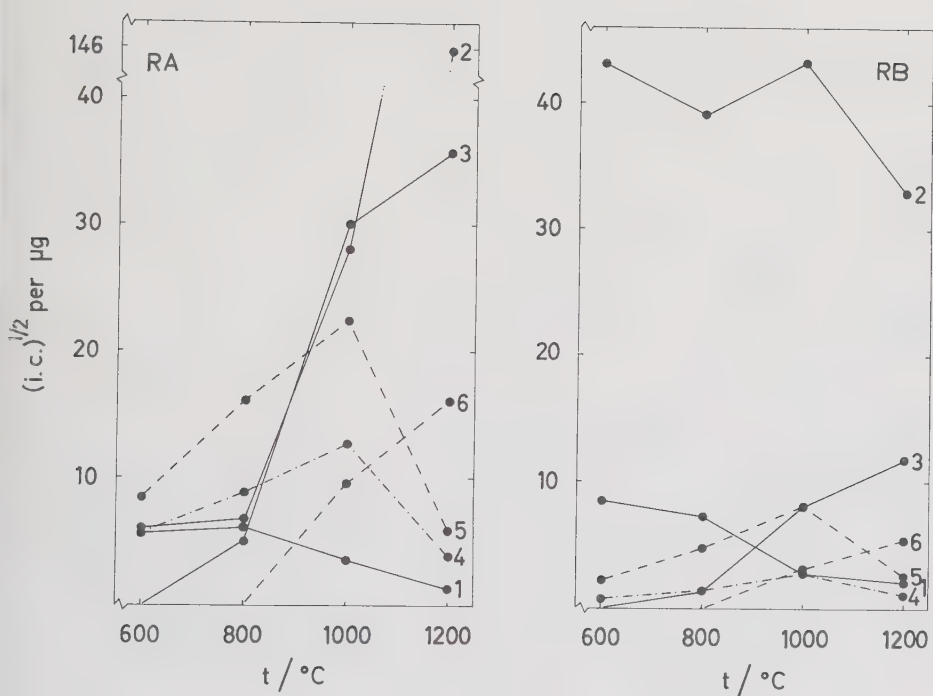


Fig. 2 The yield of the different pyrolysis products marked in Fig. 1 plotted versus the pyrolysis temperature. The samples were RA50 and sample RB 50. Pyrolysis time: 0.5 s at 600°C and 0.2 s at the other temperatures.

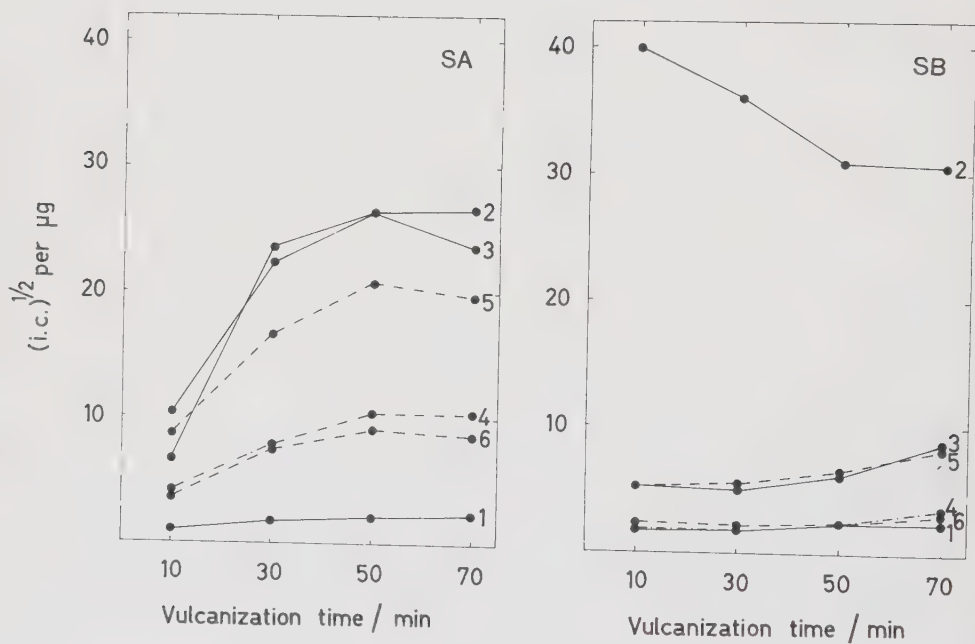


Fig. 3 The yield of the pyrolysis products marked in Fig. 1 plotted versus the vulcanization time. To the left the SA series and to the right the SB series. Pyrolysis temperature and time: 1000°C and 0.2 s.

